

DESCRIPTION

Title of Invention: LAMINATE

Technical Field

5 [0001]

The present invention relates to a laminate with excellent protection against heat. The laminate of the present invention can be used to protect various base materials in building structures from high temperatures.

10

Background Art

[0002]

When building structures are exposed to high temperatures in a fire, the physical strength of the various base materials, such as pillars, beams, floors, roofs, and walls, may drastically decrease. To address this problem, various methods have been proposed to increase heat resistance by covering the base materials in building structures with heat-resistant protective material.

20 [0003]

For example, materials containing inorganic light-weight aggregates, such as rock wool, perlite, and vermiculite, and cement are well known as heat-resistant protective materials. However, when a heat-resistant protective material containing these components is used, a thick coating with a thickness of about 20 to 50 mm needs to be applied to obtain sufficient heat resistance. This requires a large amount of material during application and imposes a great burden on work. In addition, the long period of time required for drying is also problematic. Further, the thick coating may prevent effective use of space and make the appearance of base materials oppressive.

[0004]

In recent years, a heat-resistant protective material using thermally expandable material has been drawing attention as a material that remedies the above problems. The coating of

35

thermally expandable material expands due to the temperature increase in a fire; accordingly, thermally expandable material can form a carbonized heat-insulating layer. This enables the coating in the initial stage (application stage) to be made thin.

5 [0005]

Examples of thermally expandable materials include those that for the main components contain a binder, such as polyvinyl acetate or an acrylic resin, a phosphorous compound, such as ammonium polyphosphate, a carbonizing agent, such as a polysaccharide or a polyhydric alcohol, and a nitrogen-containing foaming agent, such as melamine or dicyandiamide (Patent Literature 1, Patent Literature 2, and the like).

Citation List

15 Patent Literature

[0006]

PTL 1: JP4-504135A

PTL 2: JP7-331124A

20 Summary of Invention

Technical Problem

[0007]

However, since the thermally expandable materials disclosed in Patent Literature 1, Patent Literature 2, and the like have relatively high weight, it is desirable to reduce the weight, taking into account the work efficiency during application, the load on the building structure, etc. For example, presumably the weight would be reduced by incorporating light-weight powder; however, when light-weight powder is incorporated into the thermally expandable materials disclosed in Patent Literature 1, Patent Literature 2, and the like, the weight per unit volume is decreased, but thermal expandability may be inhibited, making it difficult to ensure excellent protection against heat.

35 [0008]

The present invention has been accomplished with the above problems taken into account, and an object of the present invention is to provide a novel laminate (heat-resistant protective material) that uses thermally expandable material and
5 in which weight reduction is achieved without impairing thinness at the initial stage, thermal expandability and protection against heat.

Solution to Problem

10 [0009]

The inventor conducted extensive research to achieve the above object and found that when a laminate comprising at least a specific thermal expansion layer A and a specific thermal expansion layer B is used, the object can be achieved. The
15 present invention has been thus accomplished.
[0010]

More specifically, the present invention relates to the following laminate.

1. A thermally expandable laminate characterized in that

20 (1) the laminate comprises at least a thermal expansion layer A and a thermal expansion layer B,

(2) the thermal expansion layer A contains a binder, a flame retardant, a foaming agent, and a carbonizing agent, and when the thermal expansion layer A further contains an inorganic
25 light-weight powder A, the content of the inorganic light-weight powder A in the thermal expansion layer A is less than 5% by volume,

(3) the thermal expansion layer B contains a binder, a flame retardant, a foaming agent, a carbonizing agent, and an
30 inorganic light-weight powder B, and the content of the inorganic light-weight powder B in the thermal expansion layer B is 5 to 70% by volume, and

(4) the inorganic light-weight powder A and the inorganic light-weight powder B each have a bulk density of 0.1
35 to 2.0 g/cm³.

2. The laminate according to item 1, which is applied to a base material of a structure that needs to be made heat-resistant, wherein the thermal expansion layer B and the thermal expansion
5 layer A are placed in this order.

3. The laminate according to item 1 or 2, wherein the thermal expansion layer A has a thickness of 0.3 to 5 mm.

10 4. The laminate according to any one of items 1 to 3, wherein the thermal expansion layer B has a thickness of 0.3 to 5 mm.

5. The laminate according to any one of items 1 to 4, wherein the inorganic light-weight powder A and the inorganic light-weight
15 powder B each have a specific surface area of not less than 0.1 m²/g.

Advantageous Effects of Invention

[0011]

20 The laminate of the present invention uses thermally expandable material. In the laminate of the present invention, weight reduction is achieved without impairing thinness at the initial stage, thermal expandability, and protection against heat. The laminate of the present invention is useful as a heat-
25 resistant protective material used for protecting various base materials in building structures from high temperatures.

Description of Embodiments

[0012]

30 The laminate of the present invention is thermally expandable and has the following features:
(1) The laminate comprises at least a thermal expansion layer A and a thermal expansion layer B;
(2) The thermal expansion layer A contains a binder, a flame
35 retardant, a foaming agent, and a carbonizing agent; and when the

thermal expansion layer A further contains an inorganic light-weight powder A, the content of the inorganic light-weight powder A in the thermal expansion layer A is less than 5% by volume;

(3) The thermal expansion layer B contains a binder, a flame retardant, a foaming agent, a carbonizing agent, and an inorganic light-weight powder B; and the content of the inorganic light-weight powder B in the thermal expansion layer B is 5 to 70% by volume; and

(4) The inorganic light-weight powder A and the inorganic light-weight powder B each have a bulk density of 0.1 to 2.0 g/cm³.

[0013]

The laminate of the present invention is preferably applied to a base material of a structure that needs to be made heat-resistant, such that the thermal expansion layer B and the thermal expansion layer A are placed in this order. More specifically, it is preferable that the thermal expansion layer B is applied closer to the base material of the structure, and that the thermal expansion layer A is applied farther from the base material of the structure. As such, in the laminate of the present invention, the side on which the thermal expansion layer B is present may be referred to as "base material side," and the side on which the thermal expansion layer A is present may be referred to as "front side." There are no limitations on base materials of structures that need to be made heat-resistant. Examples of base materials include those of building structures, such as pillars, beams, floors, roofs, and walls.

[0014]

The thermal expansion layer A on the front side has excellent thermal expandability and forms a carbonized heat-insulating layer with excellent protection against heat. The thermal expansion layer B on the base material side contributes to weight reduction and forms a strong carbonized heat-insulating layer with heat insulation to assist in the thermal expansion of the thermal expansion layer A, thus enhancing thermal expandability of the thermal expansion layer A. Further, the

thermal expansion layer B also has the effect of reinforcing the carbonized heat-insulating layer formed in the thermal expansion layer A.

[0015]

5 Since the above thermal expansion layer A and thermal expansion layer B are laminated, the laminate of the present invention is relatively light-weight and has excellent thermal expandability and excellent protection against heat.

[0016]

10 If the content of the inorganic light-weight powder B in the thermal expansion layer B on the base material side is less than 5% by volume, the weight of the laminate cannot be sufficiently reduced. In addition, it will be difficult to assist in the thermal expansion of the thermal expansion layer A and to
15 reinforce the carbonized heat-insulating layer formed in the thermal expansion layer A. If the content of the inorganic light-weight powder B is greater than 70% by volume, the strength of the thermal expansion layer B itself will be insufficient. Thus, the content of the inorganic light-weight powder B in the thermal
20 expansion layer B is defined as 5 to 70% by volume.

[0017]

 When the thermal expansion layer A on the front side contains an inorganic light-weight powder A, the content of the inorganic light-weight powder A is set to be less than 5% by
25 volume. This is because if the content of the inorganic light-weight powder A is not less than 5% by volume, thermal expandability of the thermal expansion layer A tend to be inhibited, and the formation of an excellent carbonized heat-insulating layer will be difficult.

30 [0018]

 The inorganic light-weight powders A and B each have a bulk density of 0.1 to 2.0 g/cm³, preferably 0.15 to 1.0 g/cm³, and more preferably 0.2 to 0.8 g/cm³.

[0019]

35 If the inorganic light-weight powders A and B have a

bulk density of less than 0.1 g/cm^3 , the strength of each carbonized heat-insulating layer may decrease. If the inorganic light-weight powders A and B have a bulk density of greater than 2.0 g/cm^3 , weight reduction may be difficult, and protection
5 against heat may decrease. The use of the inorganic light-weight powders A and B with bulk densities within the above ranges in the present invention enables the weight reduction of the laminate without impairing thinness at the initial stage, thermal expandability, and protection against heat. In addition, problems
10 such as sliding off of each carbonized heat-insulating layer can be prevented.

[0020]

The inorganic light-weight powders A and B are not limited as long as the predetermined bulk density requirement is
15 satisfied. Examples thereof include silica gel, zeolite, sericite, bentonite, sepiolite, vermiculite, dolomite, wollastonite, activated carbon, allophane, and the like.

[0021]

The inorganic light-weight powders A and B each have a
20 specific surface area of preferably not less than $0.1 \text{ m}^2/\text{g}$. In particular, an inorganic light-weight powder B having a specific surface area of not less than $0.1 \text{ m}^2/\text{g}$ in the thermal expansion layer B can improve heat insulation of the thermal expansion layer B. Thus, when heat is applied to the laminate, the heat
25 applied to the thermal expansion layer A is stored in the thermal expansion layer A without transferring to the thermal expansion layer B, thereby efficiently increasing the temperature of the thermal expansion layer A. As a result, the thermal expansion layer A is thermally expanded efficiently, and thus a laminate
30 with excellent protection against heat can be obtained.

[0022]

In the laminate of the present invention, the thermal expansion layer A and/or the thermal expansion layer B may contain organic light-weight powder having a bulk density of 0.1
35 to 2.0 g/cm^3 as long as the effect of the present invention is not

impaired.

[0023]

Thermal Expansion Layer A

The thermal expansion layer A, which may contain the
5 above inorganic light-weight powder A as an optional component,
contains a binder, a flame retardant, a foaming agent, and a
carbonizing agent as essential components.

[0024]

Binders used in known thermally expandable material can
10 be used as the binder. Examples of binders include organic
binders, such as acrylic resins, vinyl acetate resins, vinyl
acetate/acrylic copolymer resins, polyethylene resins,
acryl/styrene copolymer resins, vinyl acetate/ethylene copolymer
resins, polyester resins, vinyl acetate/vinyl versatate ester
15 copolymer resins, vinyl acetate/vinyl versatate ester/acrylic
copolymer resins, phenol resins, petroleum resins, vinyl chloride
resins, epoxy resins, urethane resins, polybutadiene resins,
alkyd resins, melamine resins, propylene rubbers, chloroprene
rubbers, butyl rubbers, and isobutylene rubbers. These binders
20 may be used singly or in a combination of two or more. If
necessary, inorganic binders, such as cement, gypsum, water glass,
and silicone resins, can be also used together with organic
binders.

[0025]

25 In a fire, the flame retardant exhibits at least one
effect selected from a dehydration-cooling effect, a nonflammable
gas generation effect, a binder carbonization promotion effect,
etc., to suppress the combustion of the binder. The flame
retardant is not particularly limited as long as it has such an
30 effect. The same flame retardants as those used in known
thermally expandable material may be used.

[0026]

Examples of flame retardants include organic
phosphorus-based compounds, such as tricresyl phosphate,
35 diphenyl-cresyl phosphate, diphenyl octyl phosphate, tri(β -

chloroethyl)phosphate, tributyl phosphate,
tri(dichloropropyl)phosphate, triphenyl phosphate,
tri(dibromopropyl)phosphate, chlorophosphonate, bromophosphonate,
diethyl-N,N-bis(2-hydroxyethyl)aminomethyl phosphate, and
5 di(polyoxyethylene)hydroxymethyl phosphonate; chlorine compounds,
such as chlorinated polyphenyl, chlorinated polyethylene,
diphenyl chloride, triphenyl chloride, pentachloride of fatty
acid ester, perchloropentacyclodecane, chlorinated naphthalene,
and tetrachlorophthalic anhydride; antimony compounds, such as
10 antimony trioxide and antimony pentachloride; phosphorus
compounds, such as phosphorus trichloride, phosphorus
pentachloride, ammonium phosphate, and ammonium polyphosphate;
boron compounds, such as zinc borate and sodium borate; and the
like. These flame retardants may be used singly or in a
15 combination of two or more.
[0027]

In the present invention, it is particularly preferable
to use ammonium polyphosphate as the flame retardant. When
ammonium polyphosphate is used, the dehydration-cooling effect
20 and the nonflammable gas generation effect can be more
effectively exhibited.
[0028]

The foaming agent generates nonflammable gas in a fire
to expand the binder and the carbonizing agent described below as
25 they are being carbonized, so that a carbonized heat-insulating
layer having pores can be formed. The foaming agent is not
particularly limited as long as it has this effect. The same
foaming agents as those used in known thermally expandable
material may be used.

30 [0029]

Examples of foaming agents include melamine and
derivatives thereof, dicyandiamide and derivatives thereof,
azodicarbonamide, urea, thiourea, and the like. These foaming
agents may be used singly or in a combination of two or more. Of
35 these foaming agents, melamine, dicyandiamide, azodicarbonamide,

etc., are preferable since they have excellent efficiency in generating nonflammable gas. Melamine is particularly preferred.
[0030]

The carbonizing agent carbonates the binder in a fire,
5 and the carbonizing agent itself is carbonated by dehydrogenation, thereby forming a carbonized heat-insulating layer that has sufficient thickness and excellent heat insulation. The carbonizing agent is not particularly limited as long as it has such an effect. The same carbonizing agents as those used in
10 known thermally expandable material may be used.
[0031]

Examples of carbonizing agents include polyhydric alcohols, such as pentaerythritol, dipentaerythritol, and trimethylolpropane; starch; casein; and the like. These
15 carbonizing agents may be used singly or in a combination of two or more. In particular, pentaerythritol, dipentaerythritol, etc., are preferable as the carbonizing agent in the present invention since they have an excellent dehydration-cooling effect and an excellent effect of forming a carbonized heat-insulating layer.
20 [0032]

The proportion of each component in the thermal expansion layer A is not limited as long as a carbonized heat-insulating layer with sufficient heat insulation can be formed in the event of fire. The proportion of each component in the
25 thermal expansion layer A can be set as appropriate according to the type of each component, etc.
[0033]

The proportion of the flame retardant is preferably 50 to 1000 parts by weight, more preferably 100 to 800 parts by
30 weight, and still more preferably 200 to 600 parts by weight, per 100 parts by weight of the solids content of the binder. The proportion of the foaming agent is preferably 5 to 500 parts by weight and more preferably 30 to 200 parts by weight, per 100 parts by weight of the solids content of the binder. The
35 proportion of the carbonizing agent is preferably 5 to 600 parts

by weight and more preferably 10 to 400 parts by weight, per 100 parts by weight of the solids content of the binder.

[0034]

Further, the content of the inorganic light-weight powder A in the thermal expansion layer A is 0% by volume or less than 5% by volume (preferably not greater than 3% by volume). When the thermal expansion layer A contains the inorganic light-weight powder A, the lower limit of the content of the inorganic light-weight powder A is about 1% by volume.

10 [0035]

In particular, a carbonized heat-insulating layer with excellent thermal expandability is obtained, the degree of thermal expansion is uniform, and excellent heat insulation, strength, etc., are easily obtained when the proportion of each component is within the range described above.

[0036]

The content of the inorganic light-weight powder A (% by volume) is determined by the following formula.

[0037]

20 Content of the inorganic light-weight powder A (% by volume) =
$$\frac{\text{(weight of inorganic light-weight powder A/bulk density of inorganic light-weight powder A)}}{\text{volume of thermal expansion layer A}} \times 100$$

[0038]

The thermal expansion layer A may contain, if necessary, a filler, a coloring pigment, a fiber, a plasticizer, a dispersing agent, etc., in addition to the above binder, flame retardant, carbonizing agent, foaming agent, and inorganic light-weight powder A.

[0039]

Examples of fillers include silicates, such as talc; carbonates, such as calcium carbonate and sodium carbonate; metal oxides, such as aluminium oxide, titanium dioxide, zinc oxide, and alumina; natural minerals, such as clay, clay and silica; and the like.

[0040]

35 A filler having a bulk density of greater than 2.0

g/cm³ but not greater than 3.0 g/cm³ is usually used.

[0041]

The proportion of the filler is preferably 10 to 300 parts by weight and more preferably 20 to 250 parts by weight, per 100 parts by weight of the solids content of the binder.

[0042]

Thermal Expansion Layer B

The thermal expansion layer B contains an inorganic light-weight powder B, a binder, a flame retardant, a foaming agent, and a carbonizing agent.

[0043]

The binder, flame retardant, foaming agent, and carbonizing agent used in the thermal expansion layer B may be suitably selected from the components given as examples in the Thermal Expansion Layer A section above.

[0044]

In the present invention, the use of the same or similar binder, flame retardant, foaming agent, and carbonizing agent as those used in the thermal expansion layer A makes it possible to obtain a laminate having excellent adhesion between the thermal expansion layer A and the thermal expansion layer B.

[0045]

The proportion of each component in the thermal expansion layer B is not particularly limited as long as a carbonized heat-insulating layer with sufficient heat-insulation can be formed in the event of fire. The proportion of each component in the thermal expansion layer B can be set as appropriate according to the type of each component, etc.

[0046]

The proportion of the flame retardant is preferably 50 to 1000 parts by weight, more preferably 100 to 800 parts by weight, and still more preferably 200 to 600 parts by weight, per 100 parts by weight of the solids content of the binder. The proportion of the foaming agent is preferably 5 to 500 parts by weight and more preferably 30 to 200 parts by weight, per 100

parts by weight of the solids content of the binder. The proportion of the carbonizing agent is preferably 5 to 600 parts by weight and more preferably 10 to 400 parts by weight, per 100 parts by weight of the solids content of the binder.

5 [0047]

In particular, a strong carbonized heat-insulating layer with heat insulation is formed, and thermal expandability of the thermal expansion layer A is easily enhanced, when the proportion of each component is within the range described above.

10 [0048]

Further, the content of the inorganic light-weight powder B in the thermal expansion layer B is 5 to 70% by volume (preferably 20 to 65% by volume).

[0049]

15 In particular, not only can weight reduction be achieved, but also a strong carbonized heat-insulating layer with excellent heat insulation can be formed when the content of the inorganic light-weight powder B is within the above range.

[0050]

20 The content of the inorganic light-weight powder B (% by volume) is determined by the following formula.

[0051]

Content of the inorganic light-weight powder B (% by volume) =
$$\frac{\text{(weight of inorganic light-weight powder B/bulk density of inorganic light-weight powder B)}}{\text{volume of thermal expansion layer B}} \times 100$$

25 [0052]

The thermal expansion layer B may contain, if necessary, a filler, a coloring pigment, a fiber, a plasticizer, a dispersing agent, etc., in addition to the binder, the flame retardant, the carbonizing agent, the foaming agent, and the
30 inorganic light-weight powder.

[0053]

A filler having a bulk density of greater than 2.0 g/cm³ but not greater than 3.0 g/cm³ is usually used.

[0054]

35 The proportion of the filler is preferably 10 to 300

parts by weight and more preferably 20 to 250 parts by weight,
per 100 parts by weight of the solids content of the binder.

[0055]

5 The laminate of the present invention can be applied to
a part that needs to be made heat-resistant of a structure such
as buildings and civil engineering structures. More specifically,
the laminate of the present invention can be applied to various
base materials, such as walls, pillars, floors, beams, roofs,
stairs, ceilings, doors, and other components. Examples of usable
10 materials of these components include metal, concrete, wood,
resin, and the like. These base materials may be those that have
been subjected to some kind of surface treatment (corrosion-
prevention treatment, flame-retardation treatment, etc.).

[0056]

15 As described above, the laminate of the present
invention is preferably applied to a base material of a structure
that needs to be made heat-resistant, such that the thermal
expansion layer B and the thermal expansion layer A are placed in
this order. A reinforcement layer, an adhesion layer, etc., may
20 be further disposed between the base material and the thermal
expansion layer B and/or between the thermal expansion layer B
and the thermal expansion layer A, if necessary.

[0057]

25 As the thermal expansion layer A and the thermal
expansion layer B, sheet materials that have been formed into
sheets may be used, or the thermal expansion layer A and the
thermal expansion layer B may be formed by coating. When the
thermal expansion layer A and the thermal expansion layer B are
formed by coating, a composition for each thermal expansion layer
30 (coating material) may be prepared by incorporating, as needed, a
solvent, etc., into the components described above and by
uniformly mixing the mixture according to a known method.

[0058]

35 When the thermal expansion layers are formed using
coating materials, an application area may be coated with the

coating materials by using a coating instrument, such as a sprayer, a roller, or a brush.

[0059]

When sheet materials are used, the laminate may be formed by affixing sheet materials to an application area with an adhesive, etc.

[0060]

The thickness of the laminate (dry film thickness after coating or when the thermal expansion layers are made into sheets) may be set as appropriate according to the desired heat resistance, the application area, etc. The thickness of the thermal expansion layer A is preferably 0.3 to 5 mm (further preferably, 0.4 to 4 mm), and the thickness of the thermal expansion layer B is preferably 0.3 to 5 mm (further preferably, 0.4 to 4 mm).

[0061]

In addition, a decorative layer may be formed on the surface of the laminate, if necessary.

20 Examples

[0062]

Experiments and Comparative Experiments are described below to further clarify the features of the present invention. However, the present invention is not limited to these Experiments.

(1) Preparation of Thermal Expansion Layers 1 to 12

As shown in Table 1, 100 parts by weight of a binder, 280 parts by weight of a flame retardant, 44 parts by weight of a foaming agent, 120 parts by weight of a carbonizing agent, 88 parts by weight of a filler, and 90 parts by weight of a plasticizer were uniformly mixed. Subsequently, a predetermined amount of an inorganic light-weight powder was mixed with each mixture, and each resulting mixture was heated to 120°C, kneaded with a kneader, supplied between a pair of rollers to be formed into a sheet, and then allowed to cool at room temperature,

thereby obtaining sheet-shaped thermal expansion layers.

[0063]

The type of each component is as follows.

•Binder A: acryl/styrene copolymer resin (MFR (190°C):80 g/10
5 min)

•Binder B: vinyl acetate/ethylene copolymer resin (MFR (190°C):65
g/10 min, vinyl acetate content: 41% by weight, tensile strain at
break: 1720%)

•Binder C: vinyl acetate/ethylene copolymer resin (MFR (190°C): 6
10 g/10 min, vinyl acetate content: 30% by weight, tensile strain at
break: >600%)

In the present specification, MFR is a value measured based on
JIS K7210: 1999 "Plastics - Determination of the melt mass-flow
rate (MFR) and the melt volume-flow rate (MVR) of
15 thermoplastics," at 190°C and a load of 2.16 kg.

•Flame retardant: ammonium polyphosphate

•Foaming agent: melamine

•Carbonizing agent: dipentaerythritol

•Plasticizer: chlorinated paraffin

20 •Filler: titanium oxide (rutile type, mean particle diameter of
0.3 μm , bulk density of 2.7 g/cm³)

•Inorganic light-weight powder i: wollastonite (bulk density of
0.4 g/cm³, specific surface area of 0.4 m²/g)

•Inorganic light-weight powder ii: zeolite (bulk density of 0.3
25 g/cm³, specific surface area of 350 m²/g)

[0064]

Table 1

	Thermal expansion layer											
	1	2	3	4	5	6	7	8	9	10	11	12
Binder A	100	100	100	100	100	100	100					
Binder B								100	100	100		
Binder C											100	100
Flame retardant	280	280	280	280	280	280	280	280	280	280	280	280
Foaming agent	44	44	44	44	44	44	44	44	44	44	44	44
Carbonizing agent	120	120	120	120	120	120	120	120	120	120	120	120
Filler	88	88	88	88	88	88	88	88	88	88	88	88
Plasticizer	90	90	90	90	90	90	90	90	90	90	90	90
Inorganic light-weight powder i content (% by volume)	0	2	4	30	50	60	-	0	2	30	0	30
Inorganic light-weight powder ii content (% by volume)	-	-	-	-	-	-	50	-	-	-	-	-

[0065]

- 5 All the numerical values are shown in parts by weight; however, the inorganic light-weight power content is shown in % by volume.

(2) Preparation of Test Samples and Evaluation of Their

10 Properties

For test samples of Experiments 1 to 12 and Comparative Experiments 1 to 4, in the combinations shown in Table 2, each thermal expansion layer was attached to a steel plate (150 mm × 150 mm × 6 mm) using an acrylic adhesive.

[0066]

Table 2

	Experiment								
	1	2	3	4	5	6	7	8	9
Front side (thickness(mm))	1 (0.5)	2 (0.5)	3 (0.5)	2 (0.5)	2 (0.5)	1 (0.3)	1 (0.5)	2 (0.5)	3 (0.5)
Base material side (thickness(mm))	4 (1.0)	4 (1.0)	4 (1.0)	5 (1.0)	6 (1.0)	4 (1.2)	7 (1.0)	7 (1.0)	7 (1.0)
Temperature of steel plate after 1 hour	B	B	B	A	A	C	A	A	A
Temperature of steel plate after 10 minutes	A	A	A	A	A	B	A	A	A
Detachment	II	I	I	I	I	II	II	I	I
	Experiment			Comparative Experiment					
	10	11	12	1	2	3	4		
Front side (thickness(mm))	8 (0.5)	9 (0.5)	11 (0.5)	4 (1.0)	4 (0.5)	1 (1.5)	5 (1.5)		
Base material side (thickness(mm))	10 (1.0)	10 (1.0)	12 (1.0)	6 (0.5)	6 (1.0)				
Temperature of steel plate after 1 hour	B	B	B	F	F	A	F		
Temperature of steel plate after 10 minutes	A	A	A	F	F	D	F		
Detachment	II	I	I	I	I	III	I		

[0067]

5 The upper numerical values in the row for the front side and the row for the base material side denote the type of thermal expansion layers shown in Table 1.

[0068]

Comparative Experiments 3 and 4 are each a single layer.

10 (Test of Protection against Heat)

For the obtained test samples, a heating test was performed for 1 hour in accordance with an ISO 834 standard heating curve, and the temperatures of the steel plates after 10 minutes and 1 hour were evaluated. The temperature of each steel plate refers to the temperature at the center of the rear surface of the steel plate, i.e., a surface on which no thermal expansion

15

layers were laminated.

[0069]

The evaluation method is as follows. The evaluation results are shown in Table 2.

5

Evaluation of Temperatures of Steel Plates after 10 Minutes

A: Less than 180° C

B: Not less than 180° C but less than 190° C

C: Not less than 190° C but less than 200° C

10 D: Not less than 200° C but less than 210° C

E: Not less than 210° C but less than 220° C

F: Not less than 220° C

Evaluation of Temperatures of Steel Plates after 1 Hour

15 A: Less than 480° C

B: Not less than 480° C but less than 495° C

C: Not less than 495° C but less than 510° C

D: Not less than 510° C but less than 525° C

E: Not less than 525° C but less than 540° C

20 F: Not less than 540° C

Detachment Test

Each of the obtained test samples was attached to a steel plate (70 mm × 150 mm × 1.6 mm) by using an acrylic adhesive.

25 Each obtained plate was disposed in such a manner that the surface of the test sample faced downward and the test sample was allowed to stand at 250° C for 10 minutes, and each test sample was visually evaluated for the presence of detachment and shifting. The evaluation method is as follows. The evaluation results are shown in Table 2.

30

[0070]

I: No detachment

II: Almost no detachment

III: Partial detachment of surface layer

35 IV: Completely detached

CLAIMS

[Claim 1]

A thermally expandable laminate characterized in that

5 (1) the laminate comprises at least a thermal expansion layer A and a thermal expansion layer B,

(2) the thermal expansion layer A contains a binder, a flame retardant, a foaming agent, and a carbonizing agent, and when the thermal expansion layer A further contains an inorganic
10 light-weight powder A, the content of the inorganic light-weight powder A in the thermal expansion layer A is less than 5% by volume,

(3) the thermal expansion layer B contains a binder, a flame retardant, a foaming agent, a carbonizing agent, and an
15 inorganic light-weight powder B, and the content of the inorganic light-weight powder B in the thermal expansion layer B is 5 to 70% by volume, and

(4) the inorganic light-weight powder A and the inorganic light-weight powder B each have a bulk density of 0.1
20 to 2.0 g/cm³.

[Claim 2]

The laminate according to claim 1, which is applied to a base material of a structure that needs to be made heat-
25 resistant, wherein the thermal expansion layer B and the thermal expansion layer A are placed in this order.

[Claim 3]

The laminate according to claim 1 or 2, wherein the
30 thermal expansion layer A has a thickness of 0.3 to 5 mm.

[Claim 4]

The laminate according to any one of claims 1 to 3, wherein the thermal expansion layer B has a thickness of 0.3 to 5
35 mm.

[Claim 5]

The laminate according to any one of claims 1 to 4,
wherein the inorganic light-weight powder A and the inorganic
5 light-weight powder B each have a specific surface area of not
less than $0.1 \text{ m}^2/\text{g}$.