

DESCRIPTION

TITLE OF THE INVENTION: RELEASE FILM FOR PRODUCTION OF
CERAMIC GREEN SHEET

TECHNICAL FIELD

[0001]

The present invention relates to a release film for production of a ceramic green sheet, and, in more detail, relates to a release film for production of an ultrathin ceramic green sheet, which can suppress generation of process failures due to pinholes and thickness unevenness while producing the ultrathin ceramic green sheet, and can suppress transfer of a silicone component in a release layer to the ceramic green sheet to be produced.

BACKGROUND ART

[0002]

Conventionally, a release film including a polyester film as a substrate and a release layer laminated thereon has been used for forming a ceramic green sheet for a laminated ceramic capacitor, a ceramic substrate and the like. Recently, according to decrease in size and increase in capacity of laminated ceramic capacitors, thicknesses of ceramic green sheets have tended to be reduced. A ceramic green sheet can be formed by applying slurry which contains

a ceramic component such as barium titanate and a binder resin onto a release film and then drying the slurry. After printing electrodes to the formed ceramic green sheet and peeling the ceramic green sheet from the release film, the ceramic green sheet is laminated, pressed and sintered, and external electrodes are applied to the ceramic green sheet, whereby a laminated ceramic capacitor is produced. In the case of forming a ceramic green sheet onto a surface of a release layer of a polyester film, there has been a problem that, since fine protrusions on the release layer affect the formed ceramic green sheet, defects such as cissing and pinholes are likely to be generated. Thus, various methods for realizing a surface of a release layer with excellent flatness have been developed (see, for example, Patent Documents 1 and 2).

[0003]

However, further reduction in thickness of ceramic green sheets has proceeded recently, and ceramic green sheets with thicknesses of 1.0 μm or less, particularly from 0.2 μm to 1.0 μm have been sought. As the thickness is decreased, strength of a ceramic green sheet is decreased, whereby not only flatness of a surface of a release layer but also low and uniform peel force to be applied while peeling a ceramic green sheet from a release film have been required. That is, the force applied to the

ceramic green sheet while peeling the ceramic green sheet from the release film has been more important to be decreased to lowest possible, so as not to damage the ceramic green sheet.

[0004]

Further, the silicone component in the release layer may be easily transferred to a surface of the ceramic green sheet to be produced which is in contact with the release layer. The surface, to which the silicone is transferred, obtains slipperiness, and loses adhesiveness. If using such a release film which easily transfers a silicone component to produce a ceramic green sheet, and using this ceramic green sheet further to produce a laminated ceramic product, displacement in planar direction may be generated between layers of the produced laminated ceramic product, when applying pressure to the laminated ceramic green sheets. If such displacement is generated, positional accuracy of electrodes or the like in the obtained laminated ceramic product is degraded, whereby a product performance of such a laminated ceramic product cannot be obtained. Thus, release films which transfer only small amounts of silicone components to ceramic green sheets have been sought.

[0005]

Then, a release film with a small silicone transfer

amount using: polyorganosiloxane which has at least one hydroxyl group in one molecule; and a melamine-based resin which reacts with the hydroxyl group has been proposed (see, for example, Patent Document 3). Although the silicone transfer amount is actually small, since the hydroxyl group of the polyorganosiloxane exhibits strong interaction with the melamine-based resin in a drying process, the silicone is unlikely to arise from a surface of a release layer that is to be finally obtained, so that peel force applied to a ceramic green sheet becomes high, whereby the ceramic green sheet may be damaged.

PRIOR ART DOCUMENTS

PATENT DOCUMENT

Patent Document 1: JP-A-2000-117899

Patent Document 2: WO 2013/145864

Patent Document 3: JP-A-2017-007227

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007]

The present invention has been made in the light of the above-described problems of the conventional art. That is, the present invention aims to provide a release film for production of a ceramic green sheet, in which a surface

of a release layer maintains high smoothness and exhibits low and uniform peel force, and which can form an ultrathin ceramic green sheet even with a thickness of 1 μm or less, with few defects generated, and can suppress transfer of a silicone component to the ceramic green sheet.

MEANS FOR SOLVING THE PROBLEMS

[0008]

As a result of the keen study for solving the above-described problems, the inventors of the present invention have found to provide a release film for production of a ceramic green sheet, which can suppress transfer of a silicone component to the ceramic green sheet and has excellent peelability by: adopting a polyester film; providing a release layer to at least one surface; and forming the release layer by curing a composition that contains at least a melamine-based compound and polyorganosiloxane containing a carboxyl group.

[0009]

That is, the present invention has a following structure.

1. A release film for production of a ceramic green sheet, wherein a biaxially-oriented polyester film is used as a substrate, the substrate has a surface layer A which does not substantially contain inorganic particles on at

least one surface of the substrate, a release layer is laminated onto at least one surface of the surface layer A directly or via another layer, the release layer is obtained by curing a composition containing at least a release agent and a melamine-based compound, the release agent is polyorganosiloxane containing a carboxyl group, and a content of the melamine-based compound is 80% by mass or more with respect to a solid content of the composition for forming the release layer.

2. The release film for production of a ceramic green sheet according to above 1, including: the surface layer A which does not substantially contain inorganic particles on the one surface of the substrate; and the surface layer B on a surface of the substrate opposite to the surface layer A, wherein the surface layer B contains particles, at least a part of the particles are silica particles and/or calcium carbonate particles, and a total content of the particles with respect to a mass of the surface layer B is 5000 ppm to 15000 ppm.

3. The release film for production of a ceramic green sheet according to above 1 or 2, wherein the release layer of the release film has an average area surface roughness (S_a) of 7 nm or less and a maximum protrusion height (P) of 100 nm or less.

4. A method for producing a ceramic green sheet, in

which a ceramic green sheet is formed by using the release film for production of a ceramic green sheet according to any one of above 1 to 3, wherein the formed ceramic green sheet has a thickness of 0.2 μm to 1.0 μm .

5. A method for producing a ceramic capacitor, which adopts the method for producing a ceramic green sheet according to above 4.

EFFECT OF THE INVENTION

[0010]

The release film for production of an ultrathin ceramic green sheet of the present invention includes a release layer having a smooth surface, can suppress generation of process failures due to pinholes and thickness unevenness while producing the ceramic green sheet to be less than that of the conventional release film for production of a ceramic green sheet, can suppress transfer of a silicone component in the release layer to the ceramic green sheet, and can favorably produce the ultrathin ceramic green sheet with a thickness from 0.2 μm to 1.0 μm .

MODE FOR CARRYING OUT THE INVENTION

[0011]

Hereinafter, the present invention will be described

in detail.

[0012]

The release film for production of an ultrathin ceramic green sheet of the present invention preferably includes a surface layer A which does not substantially contain inorganic particles on at least one surface of a biaxially-oriented polyester film, in which a release layer obtained by curing a composition that contains at least a melamine-based compound and polyorganosiloxane containing a carboxyl group is preferably laminated directly or via other layer onto the surface layer A.

[0013]

(Polyester film)

Polyester which constitutes the biaxially-oriented polyester film to be used as a substrate in the present invention is not limited particularly, and film-shaped polyester which is generally used as a substrate for a release film can be used, but preferably, crystalline linear saturated polyester composed of an aromatic dibasic acid component and a diol component is favorable, for example, copolymer which contains polyethylene terephthalate, polyethylene-2,6-naphthalate, polybutylene terephthalate, polytrimethylene terephthalate or any of constituent components of these resins as a main component is further favorable, and among them, a polyester film

formed of polyethylene terephthalate is particularly favorable. Polyethylene terephthalate contains a repeating unit of ethylene terephthalate preferably by 90 mol% or more and more preferably by 95 mol% or more, and may also be copolymerized with a small amount of other dicarboxylic acid component or diol component, but is preferably produced only from terephthalic acid and ethylene glycol in the light of the costs. Further, within the range not losing the effect of the film of the present invention, known additives, for example, an antioxidant, a photostabilizer, a ultraviolet absorber, a crystallizer and the like may be added. The polyester film is preferably a biaxially-oriented polyester film because of its elastic modulus in both directions and the like.

[0014]

Intrinsic viscosity of the polyethylene terephthalate film is preferably 0.50 dl/g to 0.70 dl/g, and is more preferably 0.52 dl/g to 0.62 dl/g. The intrinsic viscosity of 0.50 dl/g or more is preferable, because breaking is not generated very much in a stretching process. Whereas, 0.70 dl/g or less is preferable, because the polyethylene terephthalate film exhibits a favorable cutting property when it is cut into a predetermined product width, and a dimensional error is not generated. Further, it is preferable to dry raw material pellets sufficiently in

vacuum.

[0015]

A method for producing the biaxially-oriented polyester film of the present invention is not limited particularly, and conventionally and generally used methods can be adopted. For example, the biaxially-oriented polyester film can be obtained by: melting and extruding the polyester by an extruder into a film shape; cooling the polyester by a rotating cooling drum so as to obtain an unstretched film; and stretching the unstretched film biaxially. The biaxially-stretched film can be obtained by: a sequentially biaxially stretching method in which a uniaxially-stretched film that has been stretched in a machine direction or a transverse direction is further stretched in the transverse direction or the machine direction; or a simultaneously biaxially stretching method in which an unstretched film is stretched in the machine and transverse directions simultaneously.

[0016]

In the present invention, a stretching temperature while stretching the polyester film is preferably a secondary transition point (T_g) of polyester or more. The polyester film is stretched in each of the machine and transverse directions preferably by once to 8 times and particularly preferably by twice to 6 times.

[0017]

A thickness of the polyester film is preferably 12 μm to 50 μm , is further preferably 15 μm to 38 μm , and is more preferably 19 μm to 33 μm . The thickness of the film of 12 μm or more is preferable, because there is no risk that the film is deformed by heat during the film production or a working process of the release layer, or while forming a ceramic green sheet or the like. Whereas, the thickness of the film of 50 μm or less is preferable for saving the environmental load, because an amount of the film to be disposed after being used is not extremely large.

[0018]

The above-described biaxially-oriented polyester film substrate may be composed of a single layer or multi layers of two layers or more, but preferably has a surface layer A, which does not substantially contain inorganic particles, on at least one surface. In the case where the polyester film substrate is a laminated polyester film having a multi-layer structure composed of two layers or more, the polyester film substrate preferably has a surface layer B, which can contain particles or the like, on a surface opposite to the surface layer A that does not substantially contain inorganic particles. As the laminated structure, where a layer on which the release layer is to be applied is the surface layer A, a layer

opposite to the surface layer A is the surface layer B, and a core layer other than them is a layer C, the layer structure in a thickness direction is a laminated structure of the release layer/A/B, the release layer/A/C/B or the like. Needless to say, the layer C may be composed of plural layers. Further, the surface layer B may contain no particle. In this case, in order to add slipperiness for winding the film into a roll shape, a coat layer containing particles and a binder is preferably provided onto the surface layer B.

[0019]

In the biaxially-oriented polyester film substrate of the present invention, it is preferable that the surface layer A constituting a surface to which the release layer is applied does not substantially contain inorganic particles. In this case, average area surface roughness (S_a) of the surface layer A is preferably 7 nm or less. S_a of 7 nm or less is preferable, because pinholes and the like are not likely to be generated while forming an ultrathin ceramic green sheet to be laminated. It is more preferable as the average area surface roughness (S_a) of the surface layer A is smaller, but S_a may be 0.1 nm or more. Herein, in the case of providing a below-described anchor coat layer or the like onto the surface layer A, it is preferable that the coat layer does not substantially

contain inorganic particles, and the average area surface roughness (S_a) after laminating the coat layer satisfies the above-described range. In the present invention, "does not substantially contain inorganic particles" means that a content of the inorganic element measured by fluorescent X-ray spectroscopy is 50 ppm or less, is preferably 10 ppm or less, and is most preferably a detection limit or less. This is because, even when positively adding no inorganic particles into the film, contamination components derived from foreign substances or stains attached to raw material resins or lines or apparatuses in the processes of producing the film may be peeled off and mixed into the film.

[0020]

In the biaxially-oriented polyester film substrate of the present invention, the surface layer B constituting the surface opposite to the surface that is coated with the release layer preferably contains particles, and particularly preferably adopts silica particles and/or calcium carbonate particles, in the light of slipperiness and air releasability of the film. A content of the particles to be contained is preferably 5000 ppm to 15000 ppm as a total content of the particles in the surface layer B. At this time, average area surface roughness (S_a) of the film of the surface layer B is preferably within a

range from 1 nm to 40 nm. More preferably, Sa is within a range from 5 nm to 35 nm. In the case where the total content of the silica particles and/or the calcium carbonate particles is 5000 ppm or more and Sa is 1 nm or more, air can be released uniformly while winding the film into a roll shape, whereby the film can obtain a favorable wound shape and favorable flatness, and thus is suitable for producing an ultrathin ceramic green sheet. Further, it is preferable that the total content of the silica particles and/or the calcium carbonate particles is 15000 ppm or less and Sa is 40 nm or less, because aggregation of a lubricant is not likely to be caused, and rough protrusion is not generated, whereby quality of the ultrathin ceramic green sheet can be stable while it is produced.

[0021]

As the particles to be contained in the above-described surface layer B, other than silica and/or calcium carbonate particles, inert inorganic particles and/or heat-resistant organic particles or the like can be used. Silica and/or calcium carbonate particles are more preferably used in the light of transparency and costs, but as other adoptable inorganic particles, alumina-silica complex oxide particles, hydroxyapatite particles and the like can be exemplified. Further, as the heat-resistant

organic particles, crosslinked polyacrylic-based particles, crosslinked polystyrene particles, benzoguanamine-based particles and the like can be exemplified. Moreover, in the case of using silica particles, porous colloidal silica is preferable, and in the case of using calcium carbonate particles, light calcium carbonate which is subjected to surface treatment with a polyacrylic acid-based polymer compound is preferable in the light of prevention of fall of the lubricant.

[0022]

An average particle diameter of the particles to be added into the surface layer B is preferably $0.1\text{ }\mu\text{m}$ or more and $2.0\text{ }\mu\text{m}$ or less, and is particularly preferably $0.5\text{ }\mu\text{m}$ or more and $1.0\text{ }\mu\text{m}$ or less. The average particle diameter of the particles of $0.1\text{ }\mu\text{m}$ or more is preferable, because the slipperiness of the release film becomes favorable. Also, the average particle diameter of $2.0\text{ }\mu\text{m}$ or less is preferable, because no pinhole is generated to the ceramic green sheet by the rough particles on the release layer surface.

[0023]

The surface layer B may contain two or more kinds of particles which are made of different materials. Also, particles in the same kind with different particle diameters may be contained.

[0024]

In the case where the surface layer B does not contain particles, the surface layer B is preferably provided with slipperiness by a particle-containing coat layer provided thereon. This coating layer is not limited particularly, but is preferably provided by so-called in-line coat, which is applied while forming the polyester film. In the case where the surface layer B does not contain particles but has the particle-containing coat layer thereon, the surface of the coat layer preferably has average area surface roughness (Sa) within a range from 1 nm to 40 nm, because of the same reason as that of the above-described average area surface roughness (Sa) of the surface layer B. More preferably, Sa of the surface of the coat layer is within a range from 5 nm to 35 nm.

[0025]

For the surface layer A that is the layer to be provided with the release layer, recycled materials are not preferably used to prevent contamination of particles such as a lubricant, in the light of reducing the generation of pinholes.

[0026]

A thickness ratio of the surface layer A that is the layer to be provided with the release layer is preferably 20% or more and 50% or less with respect to a total

thickness of all layers of the substrate film. The thickness ratio of 20% or more is preferable, because influence of the particles contained in the surface layer B or the like from an inside of the film is likely to be small, and the average area surface roughness S_a can easily satisfy the above-described range. The thickness ratio of 50% or less with respect to the total thickness of the all layers of the substrate film is preferable, because a usage ratio of the recycled materials in the surface layer B can be increased, whereby an environmental load can be saved.

[0027]

Further, from the economic point of view, for the layers except for the surface layer A (the surface layer B or the above-described intermediate layer C), 50% by mass to 90% by mass of recycled materials such as film scraps and PET bottles can be used. Also in this case, a kind, an amount and a particle diameter of the lubricant contained in the surface layer B and average area surface roughness (S_a) of the surface layer B preferably satisfy the above-described ranges.

[0028]

Moreover, in order to improve adhesiveness of the release layer to be applied later, and prevent electrification and the like, the surface(s) of the surface layer A and/or the surface layer B may be provided with a

coat layer(s) on the unstretched or uniaxially-stretched film in the film formation process, and can also be subjected to corona treatment and the like.

[0029]

(Structure of release layer)

The release layer of the present invention is preferably formed by curing a composition containing at least a melamine-based compound and polyorganosiloxane that contains a carboxyl group. Within the range not losing the effect of the film of the present invention, other components than the resin or the additives can also be added.

[0030]

The melamine-based compound to be used for the release layer of the present invention is not limited particularly, and general melamine-based compounds can be used, but a preferable melamine-based compound is obtained by condensing melamine and formaldehyde, and has one or more of triazine rings and methylool groups and/or alkoxymethyl groups respectively in one molecule. More specifically, an etherified compound obtained by causing a dehydration condensation reaction of a methylool melamine derivative, which is obtained by condensing melamine and formaldehyde, with methyl alcohol, ethyl alcohol, isopropyl alcohol, butyl alcohol or the like as lower alcohol and the

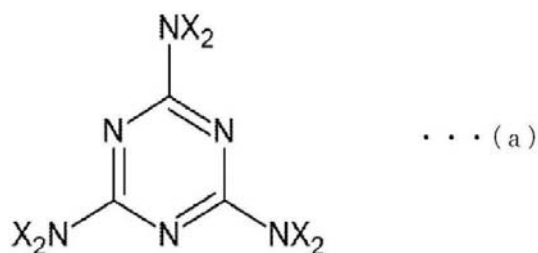
like are preferable. As the methylolated melamine derivative, for example, monomethylol melamine, dimethylol melamine, trimethylol melamine, tetramethylol melamine, pentamethylol melamine and hexamethylol melamine can be exemplified. One kind alone may be used, or two kinds or more may be used.

[0031]

The release layer of the present invention preferably have high crosslink density and high elastic modulus in order to suppress deformation of the release layer, which is caused while it is peeled, and to allow peel force to be low and uniform. Thus, hexamethylol melamine and hexaalkoxymethyl melamine which have more crosslinking points in one molecule are preferably used, hexaalkoxymethyl melamine having higher reactivity is more preferably used, and hexamethoxymethyl melamine is particularly preferably used. At this time, hexamethylol melamine is a compound represented by a below formula (a), in which X is a methylol group ($-\text{CH}_2-\text{OH}$). Hexaalkoxymethyl melamine is obtained by a dehydration condensation reaction of a methylol melamine derivative using alcohol, and is a compound in which X is ($-\text{CH}_2-\text{OR}$, where R is a 1-4C alkyl group). Hexamethoxymethyl melamine is a compound in which X is ($-\text{CH}_2-\text{OMe}$).

[0032]

[Formula 1]



[0033]

Respective X in the above-described (a) may be the same or different. Also, above-described respective R may be the same or the different. Further, X may also be (-H).

[0034]

The melamine-based compound to be used for the release layer of the present invention has weight average molecular weight which is preferably 250 or more and 1000 or less. The weight average molecular weight is more preferably 250 or more and 900 or less, and further preferably 300 or more and 800 or less. The weight average molecular weight of 1000 or less is preferable, because a crosslinking reaction is likely to proceed, so that a film with higher crosslink density can be formed, whereby peel force can be low. The weight average molecular weight of 250 or more is preferable, because the crosslink density is not increased excessively, whereby curls are not deteriorated. Incidentally, the weight average molecular

weights in the present specification are values obtained in terms of standard polystyrene conversion by gel permeation chromatography (GPC).

[0035]

The weight average molecular weight of the melamine-based compound ranging from 250 to 1000 means that a large amount of a mononuclear body is contained in the melamine-based compound to be used in the present invention. The mononuclear body has more crosslinking points and higher reactivity than those of a multinuclear body which is obtained by condensing two or more melamine derivatives, and thus can compose a release layer having higher crosslink density and excellent peelability. It is more preferable as a content of the mononuclear body is higher, and the melamine-based compound made only of the mononuclear body is most preferably used.

[0036]

The weight average molecular weight can also be represented by a weight average polymerization degree. A weight average polymerization degree of the melamine-based compound to be used is preferably 2.0 or less, and is more preferably 1.5 or less, and the melamine-based compound with a lower weight average polymerization degree can be used more favorably. The weight average polymerization degree of 2.0 or less is preferable, because the content of

the mononuclear body in the melamine-based compound is high, whereby the release layer can be provided with excellent reactivity and peelability. Incidentally, the weight average polymerization degrees in the present specification are values calculated in terms of standard polystyrene conversion from weight average molecular weight by gel permeation chromatography.

[0037]

In a process of synthesizing a melamine-based compound, a compound containing an imino group ($-\text{NH}_2-$) and a multinuclear body may be mixed. Even if these melamine derivatives are mixed, as far as the weight average polymerization degrees of the melamine-based compounds are within the above-described range, the melamine-based compounds have excellent reactivity, and thus can be used favorably.

[0038]

The release layer of the present invention contains the melamine-based compound preferably by 80% by mass or more and 99.9% by mass or less, more preferably by 90% by mass or more and 99.9% by mass or less, and further preferably by 95% by mass or more and 99.9% by mass or less with respect to a solid content of a release layer-forming composition. By containing the melamine-based compound by 80% by mass or more, the release layer can obtain high

crosslink density by self crosslinking of the melamine-based compound, and can suppress the deformation of the release layer during the peeling. At this time, it can be acknowledged that the solid content of the release layer-forming composition is substantially a sum of solid contents of the melamine-based compound and a release agent, because a solvent and an acid catalyst are mostly evaporated in the drying process.

[0039]

To the release layer of the present invention, an acid catalyst is preferably added so as to promote the crosslinking reaction of the melamine-based compound, and the release layer-forming composition, to which the acid catalyst is added, is preferably applied and cured. The acid catalyst to be used is not limited particularly, and existing acid catalysts may be used, but a sulfonic acid-based catalyst is preferably used.

[0040]

As the sulfonic acid-based catalyst, for example, p-toluenesulfonic acid, xylenesulfonic acid, cumenesulfonic acid, dodecylbenzenesulfonic acid, dinonylnaphthalenesulfonic acid, trifluoromethanesulfonic acid and the like can be suitably used, but in the light of the reactivity, p-toluenesulfonic acid can be particularly suitably used.

[0041]

As the sulfonic acid-based catalyst to be used in the present invention, commercially available sulfonic acid-based catalysts may also be used. Examples of the commercially available products include DRYER (Registered Trademark) 900 (p-toluenesulfonic acid, produced by Hitachi Chemical Co., Ltd.), NACURE (Registered Trademark) DNNSA series (dinonylnaphthalenedisulfonic acid, produced by Kusumoto Chemicals, Ltd.), NACURE DNNSA series (dinonylnaphthalene(mono)sulfonic acid, produced by Kusumoto Chemicals, Ltd.), NACURE DDBSA series (dodecylbenzenesulfonic acid, produced by Kusumoto Chemicals, Ltd.), NACURE p-TSA series (p-toluenesulfonic acid, produced by Kusumoto Chemicals, Ltd.) and the like.

[0042]

The sulfonic acid-based catalyst has higher acidity and reactivity than those of other acid catalysts such as a carboxylic acid-based catalyst, whereby the release layer can be processed at a lower temperature. Thus, deterioration of flatness and winding appearance of the film, which are caused by heat applied during the processing, can be suppressed, whereby the sulfonic acid-based catalyst is preferable.

[0043]

An adding amount of the acid catalyst is preferably

from 0.1% by mass to 10% by mass with respect to the content of the melamine-based compound contained in the release layer. The adding amount is more preferably 0.5% by mass to 8% by mass, and is further preferably 0.5% by mass to 5% by mass. The adding amount of 0.1% by mass or more is preferable, because the curing reaction is likely to proceed. Whereas, the adding amount of 10% by mass or less is preferable, because the acid catalyst is unlikely to transfer to or adversely affect a ceramic green sheet to be formed.

[0044]

As the release agent (an additive for improving the releasability of the release layer) to be used for the release layer of the present invention, in order to realize both of the releasability and the suppress of the transfer amount, polyorganosiloxane containing a carboxyl group is preferably used. Polyorganosiloxane containing a carboxyl group, which has a polydimethylsiloxane structure (abbreviated as PDMS) among polyorganosiloxane structures, can be suitably used.

[0045]

Since the polyorganosiloxane which is the release agent contains a carboxyl group, the release agent does not exhibit any strong interaction with the melamine-based compound in the drying process, and is likely to be

oriented to the surface of the release layer, thereby obtaining favorable releasability. Thus, using the polyorganosiloxane containing a carboxyl group is preferable, because the satisfactory releasability can be obtained even with a small amount of the release agent. Also, it is preferable that the polyorganosiloxane which is the release agent contains a carboxyl group, because the polyorganosiloxane exhibits weak interaction with the melamine-based compound, and it is known that the transfer to the ceramic green sheet is unlikely to occur.

[0046]

The carboxyl group may be introduced to one terminal, both terminals or a side chain of the polyorganosiloxane, but the polyorganosiloxane with one terminal to which the carboxyl group is introduced is more preferable, because of its excellent peelability. Further, the number of position(s) to be introduced may be one or plural.

[0047]

The carboxyl group-modified polyorganosiloxane may be polyorganosiloxane in which a carboxyl group is bonded directly to a silicon atom, or may also be polyorganosiloxane to which a carboxyl group is bonded via an alkyl group or an aryl group. However, polyorganosiloxane to which a carboxyl group is bonded via an organic group having a repeating unit such as polyether,

polyester and polyurethane is not preferable very much.

[0048]

A functional group to be introduced to the polyorganosiloxane which is the release agent may have other functional group than a carboxyl group in one molecule, but only a carboxyl group is more preferable. Other functional group than the carboxyl group is not preferably contained, because intermolecular interaction with the melamine-based compound is increased more than necessity, whereby the polyorganosiloxane may be unlikely to be oriented to the surface of the release layer.

[0049]

The polyorganosiloxane modified with a hydroxyl group or the like which exhibits strong intermolecular interaction with a melamine-based compound reacts with the melamine-based compound rapidly in the drying process, and thus may be unlikely to be oriented to the surface of the release layer, whereby the releasability may be unlikely to be exhibited. Thus, it is necessary to increase an adding amount thereof to provide sufficient releasability, but in this case, elastic modulus of the release layer is decreased, and the release layer is likely to be deformed during the peeling, whereby the peel force is afraid to be increased. Also, it is not preferable to increase the adding amount of the polyorganosiloxane, because the

transfer amount thereof to a ceramic green sheet tends to be increased.

[0050]

The polyorganosiloxane containing a carboxyl group to be used in the present invention preferably has molecular weight of 40000 or less. The molecular weight is more preferably 30000 or less, and is further preferably 10000 or less, and polyorganosiloxane having lower molecular weight can be used more preferably. The molecular weight of 40000 or less is preferable, because the polyorganosiloxane containing a carboxyl group is likely to be segregated to the surface of the release layer, and exhibits excellent releasability.

[0051]

As described above, the polyorganosiloxane containing a carboxyl group is more preferably polydimethylsiloxane containing a carboxyl group. As the polydimethylsiloxane containing a carboxyl group, X22-3701E (polydimethylsiloxane with a side chain carboxyl-modified, produced by Shin-Etsu Chemical Co., Ltd.), X22-3710 (polydimethylsiloxane with one terminal carboxyl-modified, produced by Shin-Etsu Chemical Co., Ltd.), X22-162C (polydimethylsiloxane with both terminals carboxyl-modified, produced by Shin-Etsu Chemical Co., Ltd.), BY16-750 (polydimethylsiloxane with both terminals carboxyl-

modified, produced by Dow Corning Toray Co., Ltd.), BY16-880 (polydimethylsiloxane with a side chain carboxyl-modified, produced by Dow Corning Toray Co., Ltd.), Magnasoft 800L (polydimethylsiloxane with both terminals carboxyl-modified, produced by Momentive Performance Materials Inc.) and the like can be used.

[0052]

As the polydimethylsiloxane containing a carboxyl group of the present invention, an acrylic resin in which polydimethylsiloxane is introduced as a side chain to an acrylic main chain containing the carboxyl group may also be used. As the acrylic resin in which polydimethylsiloxane is introduced as a side chain to an acrylic main chain containing the carboxyl group, SYMAC (Registered Trademark) US-350, US-352, US-380 (produced by TOAGOSEI CO., LTD.) and the like can be used. Also, the acrylic resin in which polydimethylsiloxane is introduced as a side chain to an acrylic main chain containing a carboxyl group and a hydroxyl group in one molecule may be used. As the acrylic resin in which polydimethylsiloxane is introduced as a side chain to an acrylic main chain containing a carboxyl group and a hydroxyl group in one molecule, SYMAC (Registered Trademark) US-450, US-480 (produced by TOAGOSEI CO., LTD.) and the like can be used.

[0053]

The release layer of the present invention preferably contains the release agent by 0.1% by mass or more and 20% by mass or less with respect to the solid content of the release layer-forming composition. The content is more preferably 0.1% by mass or more and 10% by mass or less, and is further preferably 0.1% by mass or more and 5% by mass or less. The content of 0.1% by mass or more is preferable, because the releasability can be improved, and the peelability of a ceramic green sheet can also be improved. Whereas, the content of 20% by mass or less is preferable, because the elastic modulus of the release layer is not decreased excessively, and the increase of the peel force caused due to the deformation of the release layer while peeling a ceramic green sheet can be suppressed. Further, the content of 20% by mass or less is preferable, also because the transfer amount of the release agent becomes not too high. At this time, it can be acknowledged that the solid content of the release layer-forming composition is substantially a sum value of solid contents of the melamine-based compound and the release agent, because a solvent and an acid catalyst are mostly evaporated in the drying process.

[0054]

The release layer of the present invention can contain particles with a particle diameter of 1 μm or less

and the like, but does not preferably contain particles or the like which forms protrusions, in the light of the generation of pinholes.

[0055]

Within the range not losing the effect of the present invention, additives such as an adhesion improving agent and an anti-static agent may be added into the release layer of the present invention. Further, in order to improve the adhesiveness with the substrate, a surface of the polyester film is preferably subjected to pretreatment such as anchor coating, corona treatment, plasma treatment and atmospheric plasma treatment, before being provided with a release-coated layer.

[0056]

(Property of release layer)

In the present invention, a thickness of the release layer is not limited particularly, and may be set according to its purpose of use, but is within a range that provides weight of a release-coated layer after cure to be preferably 0.01 μm to 2.0 μm , more preferably 0.01 μm to 1.0 μm , further preferably 0.01 μm to 0.8 μm , still further preferably 0.02 μm to 0.5 μm , and most preferably 0.02 μm to 0.3 μm . The thickness of the release layer of 0.01 μm or more is preferable because a peeling function can be obtained. Further, the thickness of the release layer of

2.0 μm or less is preferable, because a curing time can be shorter, and flatness of the release film can be maintained, whereby thickness unevenness of a ceramic green sheet can be suppressed.

[0057]

The release layer surface of the release film of the present invention is preferably flat so as not to generate defects to a ceramic green sheet which is to be applied and formed thereon, and it is preferable that average area surface roughness (S_a) of the release layer surface is 7 nm or less and a maximum protrusion height (P) thereof is 100 nm or less. Further, it is more preferable that the average area surface roughness is 5 nm or less, and the maximum protrusion height is 80 nm or less. The average area surface roughness of 7 nm or less and the maximum protrusion height of 100 nm or less is preferable, because defects such as pinholes are not generated while forming the ceramic green sheet, thereby obtaining a favorable yield. It is more preferable that the average area surface roughness (S_a) is smaller, but may be 0.1 nm or more, and may be 0.3 nm or more. It is also preferable that the maximum protrusion height (P) is smaller, but may be 1 nm or more, and may be 3 nm or more.

[0058]

The release film of the present invention adopts a

substrate film that is highly flattened, and thus can allow the surface of the release layer to be smooth, even if a thickness of the release layer is decreased to less than 0.5 μm and further to less than 0.2 μm . Thus, even the release layer using the melamine-based compound with high reactivity can suppress the generation of curls. Further, amounts of a solvent and resins to be used can be saved, whereby the release film for production of an ultrathin ceramic green sheet can be produced eco-friendly at low costs.

[0059]

Surface free energy (γ_s) on the surface of the release layer of the release layer film of the present invention is preferably 18 mJ/m^2 or more and 35 mJ/m^2 or less. The surface free energy (γ_s) is more preferably 23 mJ/m^2 or more and 35 mJ/m^2 or less, and is further preferably 23 mJ/m^2 or more and 30 mJ/m^2 or less. The surface free energy (γ_s) of 18 mJ/m^2 or more is preferable, because cissing is unlikely to be generated while applying ceramic slurry, whereby the ceramic slurry can be applied uniformly. Also, the surface free energy (γ_s) of 35 mJ/m^2 or less is preferable, because the releasability of a ceramic green sheet is unlikely to be decreased. By setting the surface free energy (γ_s) within the above-described range, cissing is unlikely to be generated during

the coating, whereby the release film having excellent releasability can be provided.

[0060]

Peel force of the release film of the present invention applied while peeling a ceramic green sheet is preferably 0.5 mN/mm^2 or more and 2.5 mN/mm^2 or less. The peel force is more preferably 0.8 mN/mm^2 or more and 2.0 mN/mm^2 or less. The peel force of 0.5 mN/mm^2 or more is preferable, because the peel force is not too low and the ceramic green sheet is unlikely to be lifted off while it is conveyed. The peel force of 2.5 mN/mm^2 or less is preferable, because the ceramic green sheet is not likely to be damaged while it is peeled.

[0061]

A curl of the release film of the present invention after being heated at 100°C for 15 minutes with no tension applied is preferably 3 mm or less, and is more preferably 1 mm or less. Needless to say, it is also preferable that the release film is not curled at all. The curl of 3 mm or less is preferable, because the curl is small when forming a ceramic green sheet and printing electrodes thereon, and printing precision can be enhanced.

[0062]

It is more preferable that a transfer amount of a silicone component of the release film of the present

invention to the ceramic green sheet after it is peeled is smaller. The transfer amount of the silicone component can be evaluated by: applying and forming PVB, which is one kind of binder components contained in the ceramic green sheet, onto the release film simulatively; and measuring Si intensity of the release layer before and after peeling the PVB by fluorescent X-ray. More specifically, where the Si intensity of the surface of the release layer is denoted by Si (before), and the Si intensity of the release surface of the release film after applying and peeling the PVB sheet is denoted by Si (after), a value of Si (before) - Si (after) is denoted as the transfer amount. This transfer amount is preferably 0.10 kcps or less, and is more preferably 0.04 kcps or less. The transfer amount of 0.10 kcps or less is preferable, because generation of process failures such as laminate displacement and poor bonding can be suppressed, and reliability of a ceramic capacitor is unlikely to be degraded.

[0063]

In the present invention, a method for forming the release layer is not limited particularly, and a method of: expanding coating liquid, in which a releasable resin is dissolved or dispersed, onto one of surfaces of the polyester film of the substrate by coating or the like; removing a solvent and the like by drying; drying by heat;

and curing by heat can be adopted. At this time, drying temperatures during the solvent drying and the heat curing is preferably 100°C or more and 180°C or less, is more preferably 100°C or more and 160°C or less, and is most preferably 100°C or more and 140°C or less. A heating time thereof is preferably 30 seconds or less, and is more preferably 20 seconds or less. The temperature of 180°C or less is preferable, because the flatness of the film can be maintained, and thickness unevenness of a ceramic green sheet is less likely to be caused. The temperature of 140°C or less is particularly preferable, because the processing can be carried out without losing the flatness of the film, and the thickness unevenness of the ceramic green sheet is further unlikely to be caused. The temperature of less than 100°C is not preferable, because the curing reaction of the melamine does not proceed sufficiently, and the elastic modulus of the release layer is decreased.

[0064]

In the present invention, surface tension of the coating liquid while being applied onto the release layer is not limited particularly, but is preferably 30 mN/m or less. By setting the surface tension as described above, wettability after being coated is improved, and unevenness on a surface of a coating film after being dried can be

reduced.

[0065]

In the present invention, a solvent having a boiling point of 90°C or more, which is not limited particularly, is preferably added into the coating liquid when being applied as the release coating layer. By adding the solvent having the boiling point of 90°C or more, explosive boil during the drying can be prevented, and the coating film can be levelled, whereby the smoothness of the surface of the coating film after being dried can be improved. An adding amount thereof is preferably about 10% by mass to about 80% by mass with respect to a total amount of the coating liquid.

[0066]

As a method for applying the coating liquid, known arbitrary coating methods can be adopted, and conventionally known methods, for example, roll coating such as gravure coating and reverse coating, bar coating such as wire bar, die coating, spray coating, air knife coating and the like can be used.

[0067]

(Ceramic green sheet and ceramic capacitor)

Generally, a laminated ceramic capacitor has a rectangular parallelopiped ceramic body. Inside the ceramic body, first internal electrodes and second internal

electrodes are provided alternately along a thickness direction. The first internal electrode is exposed from a first end face of the ceramic body. On the first end face, a first external electrode is provided. The first internal electrode is electrically connected to the first external electrode via the first end face. The second internal electrode is exposed from a second end face of the ceramic body. On the second end face, a second external electrode is provided. The second internal electrode is electrically connected to the second external electrode on the second end face.

[0068]

The release film for production of an ultrathin ceramic green sheet of the present invention is used for producing such a laminated ceramic capacitor. For example, a laminated ceramic capacitor can be produced as follows. Firstly, ceramic slurry for structuring the ceramic body is applied to the release film of the present invention, which is used as a carrier film, and is dried. Ceramic green sheets as ultrathin products with thicknesses of 0.2 μm to 1.0 μm have been sought. On the applied and dried ceramic green sheet, a conductive layer for structuring the first or second internal electrode is printed. The ceramic green sheet; the ceramic green sheet on which the conductive layer for structuring the first internal electrode is

printed; and the ceramic green sheet on which the conductive layer for structuring the second internal electrode is printed are laminated as appropriate, and are pressed, thereby obtaining a mother laminated body. By cutting the mother laminated body into plural pieces so as to produce a raw ceramic body. By sintering the raw ceramic body, a ceramic body is obtained. Thereafter, by forming the first and second external electrodes, a laminated ceramic capacitor can be produced completely.

EXAMPLES

[0069]

Hereinafter, the present invention will be described in more detail by way of examples, but the present invention is not limited at all by these examples. Characteristic values used in the present invention were evaluated by below-described methods.

[0070]

(Surface roughness)

Surface Roughness are values obtained by measurement using a noncontact surface shape measurement system (VertScan R550H-M100) under below-described conditions. As average area surface roughness (Sa), an average value of five measurement values was adopted, and as a maximum protrusion height (P), a value that was largest among five

measurement values, which were obtained by excluding a maximum value and a minimum value from seven measurement values, was used.

(Measurement conditions)

- Measurement Mode: WAVE Mode
- Objective Lens: 10 Times
- 0.5 × Tube Lens
- Measurement Area 936 μm × 702 μm

(Analysis conditions)

- Plane correction: Fourth Correction
- Interpolation Processing: Complete Interpolation

[0071]

(Surface free energy)

Using a contact angle meter (produced by Kyowa Interface Science Co., Ltd., a fully automatic contact angle meter DM-701) under conditions at 25°C and 50% RH, contact angles of droplets of water (droplet amount of 1.8 μL), diiodomethane (droplet amount of 0.9 μL) and ethylene glycol (droplet amount of 0.9 μL), which were formed on a release surface of a release film, were measured. As the contact angle, a contact angle after 10 seconds from dropping each liquid onto the release film was adopted. The contact angle data of water, diiodomethane and ethylene glycol obtained by the above-described method was calculated based on "Kitazaki-Hata" theory so as to obtain

a dispersion component γ_{sd} , a polar component γ_{sp} and a hydrogen bond component γ_{sh} of surface free energy of the release film, and the respective components were summed, thereby obtaining the surface free energy γ_s . For this calculation, a calculation software in this contact angle meter software (FAMAS) was used.

[0072]

(Coating property evaluation of ceramic slurry)

A composition containing below-described materials was stirred to be mixed and dispersed with zirconia beads having a diameter of 0.5 mm for 30 minutes by using a bead mill, thereby obtaining ceramic slurry.

Toluene	76.3 Parts by Mass
Ethanol	76.3 Parts by Mass
Barium Titanate (Produced by FUJI TITANIUM INDUSTRY CO., LTD., HPBT-1)	35.0 Parts by Mass
Polyvinylbutyral (Produced by SEKISUI CHEMICAL CO., LTD., S-LEC BM-S)	3.5 Parts by Mass
DOP (Dioctyl Phthalate)	1.8 Parts by Mass

Subsequently, the slurry was applied onto a release surface of the obtained release film sample by using an applicator so that the slurry after being dried might be 1 μm , and then was dried at 90°C for 1 minute, and a coating property was evaluated according to following criteria.

○: Cissing was not found, and the entire surface was coated.

△: Cissing was slightly found at ends of coated parts, but almost the entire surface was coated.

×: Cissing was found in many parts, and the surface was not coated.

[0073]

(Pinhole evaluation of ceramic green sheet)

A ceramic green sheet with a thickness of 1 μm was formed on a release surface of the release film, similarly to that in the coating property evaluation of the ceramic slurry. Subsequently, the release film was peeled off from the formed ceramic green sheet which was attached to the release film, thereby obtaining the ceramic green sheet. Light was shed onto a range of 25 cm^2 in a central region along a film transverse direction of a surface of the obtained ceramic green sheet, from an opposite side of the ceramic slurry-coating surface, and a condition of generation of pinholes was observed by transmission of light, thereby performing pinhole evaluation by visual observation according to following criteria.

○: Generation of no pinhole was observed.

△: Generation of almost no pinhole was observed.

×: Generation of many pinholes were observed.

[0074]

(Peelability evaluation of ceramic green sheet)

A composition containing below-described materials was stirred to be mixed and dispersed with zirconia beads having a diameter of 0.5 mm for 60 minutes by using a bead mill, thereby obtaining ceramic slurry.

Toluene	38.3 Parts by Mass
Ethanol	38.3 Parts by Mass
Barium Titanate (Produced by FUJI TITANIUM INDUSTRY CO., LTD., HPBT-1)	64.8 Parts by Mass
Polyvinylbutyral (Produced by SEKISUI CHEMICAL CO., LTD., S-LEC BM-S)	6.5 Parts by Mass
DOP (Dioctyl Phthalate)	3.3 Parts by Mass

Subsequently, the slurry was applied onto a release surface of the obtained release film sample by using an applicator so that the slurry after being dried might have a thickness of 10 μm , and then was dried at 90°C for 1 minute, thereby forming a ceramic green sheet on the release film. The obtained release film with the ceramic green sheet attached thereto was destaticized by a static eliminator (produced by KEYENCE CORPORATION, SJ-F020), and was subsequently peeled off to have a width of 30 mm at a peel angle of 90° and peel speed of 10 m/min. Stress applied during the peeling was measured, and was denoted as peel force. Peelability was evaluated from the obtained

value of the peel force according to following criteria.

○: 0.5 mN/mm² or More and 2.0 mN/mm² or Less

△: More Than 2.0 mN/mm² and 2.5 mN/mm² or Less

×: More Than 2.5 mN/mm²

[0075]

(Evaluation of silicone component transfer amount of release layer)

A composition containing below-described materials was stirred to be mixed, thereby obtaining polyvinylbutyral (PVB) solution.

Toluene	45.0 Parts by Mass
Ethanol	45.0 Parts by Mass
Polyvinylbutyral (Produced by SEKISUI CHEMICAL CO., LTD., S-LEC BM-S)	10.0 Parts by Mass

Subsequently, the solution was applied onto a release surface of the obtained release film sample by using an applicator so that a polyvinylbutyral (PVB) sheet after being dried might be 10 μm, and then was dried at 90°C for 1 minute, thereafter, the release film was peeled off, and Si intensity of a surface (release layer) of the peeled PVB sheet, which had been in contact with the release film, and the release layer of the release film before being coated with the PVB sheet were measured by a fluorescent X-ray apparatus (ZSX Primus II produced by Rigaku Corporation),

thereby determining a transfer amount of the silicon component. Measurement conditions of the fluorescent X-ray apparatus were as follows.

Analysis ray: Si-KA, Target: Rh 4.0kW

Tube Voltage: 50 kV, Tube Current: 60 mA

Filter: OUT, Attenuator: 1/1, Slit: S4,

Dispersive Crystal: PET

Detector: PC, PHA Condition: 100 (Lower Limit) -
300 (Upper limit)

Measurement Diameter: 30 mm, Atmosphere: Vacuum

The transfer amount of the silicone component denotes a value obtained by subtracting Si (after) from Si (before), where Si (before) denotes the Si intensity on the release surface of the release film before applying the PVB sheet, and Si (after) denotes the Si intensity on the release surface of the release film after applying and peeling off the PVB sheet. Evaluation was performed from the obtained value of the transfer amount of the silicone component according to following criteria.

○: 0.04 kcps or Less

△: More Than 0.04 kcps and Less Than 0.10 kcps

×: 0.10 kcps or More

[0076]

(Curl evaluation of release film)

The release film sample was cut into a size of 10 cm

× 10 cm, and was treated by heat at 100°C for 15 minutes in a heat air oven so that tension might not be applied to the release film. Thereafter, the release film sample was taken out from the oven, was cooled to a room temperature, and was put on a glass plate so that its release surface might be face-up, and heights of four corners that rose from the glass plate were measured. An average value of the thus measured rising quantities at the four corners was denoted as a curl amount. Evaluation of the curling property was performed according to following criteria.

⊙: Curl was 1 mm or less, and almost no curl was found.

○: Curl was more than 1 mm and 3 mm or less, and slight curls were found.

△: Curl was more than 3 mm and 10 mm or less, and curls were found.

×: Curl was more than 10 mm.

[0077]

(Method for measuring weight average polymerization degree)

Analysis Conditions

A sample was weighed by 16 mg, and was dissolved into 8 ml of chloroform. The solution was filtered with a membrane filter of 0.2 μm, and the obtained sample solution was subjected to gel permeation chromatography (GPC) analysis under following conditions.

Apparatus: TOSOH HLC-8320GPC

Column: K-G+ K-802 (Elimination Limit Molecular Weight of 5×10^3) + K-801 (Elimination Limit Molecular Weight of 1.5×10^3) (Shodex),

Solvent: Chloroform 100%

Flow Rate: 1.0 ml/min

Concentration: 0.2%

Injection Volume: 50 μ L

Temperature: 40°C

Detector: RI

Weight average molecular weight was calculated based on polystyrene conversion, and a weight average polymerization degree was calculated from the obtained value. As the polystyrene, PStQuick C (TOSOH) in PStQuick series was used. Among polystyrene added as PStQuick C (TOSOH), polystyrene Mw 2110000, 427000 and 37900, which was largely beyond the elimination limit molecular weight of the column, was excluded from formation of a calibration curve.

[0078]

(Preparation of polyethylene terephthalate pellet (PET (I)))

As an esterification reactor, a consecutive esterification reactor constituted of three-stage completely mixing tanks, which has a stirring device, a

partial condenser, a raw material inlet and a product outlet, was used. Slurry of: TPA (terephthalic acid) in an amount of 2 tons/hour; EG (ethylene glycol) in an amount of 2 mol per 1 mol of TPA; and antimony trioxide in an amount for providing 160 ppm of Sb atoms with respect to PET to be generated was continuously supplied into a first esterification reactor vessel of the esterification reactor, and was reacted at 255°C at normal pressure for an average retention time of 4 hours. Subsequently, a reaction product in the first esterification reactor vessel was continuously taken out of the system, and was supplied into a second esterification reactor vessel, and then, EG distilled from the first esterification reactor vessel was supplied into the second esterification reactor vessel by 8% by mass with respect to the PET to be generated, and further, EG solution containing magnesium acetate tetrahydrate by an amount for providing 65 ppm of Mg atoms with respect to the PET to be generated and EG solution containing TMPA (trimethylphosphate) by an amount for providing 40 ppm of P atoms with respect to the PET to be generated were added, and they were reacted with each other at 260°C at normal pressure for an average retention time of 1 hour. Subsequently, a reaction product in the second esterification reactor vessel was continuously taken out of the system, and was supplied into a third esterification

reactor vessel, and while 0.2% by mass of porous colloidal silica with an average particle diameter of 0.9 μm , which was subjected to dispersion treatment at pressure of 39 MPa (400 kg/cm²) by an average treatment times of 5 passes by using a high pressure disperser (produced by Nippon Seiki Co., Ltd.), and 0.4% by mass of synthetic calcium carbonate with an average particle diameter of 0.6 μm , to which an ammonium salt of polyacrylic acid was attached by 1% by mass with respect to the calcium carbonate, were added respectively as 10% EG slurry to the third esterification reactor vessel, they reacted with each other at 260°C at normal pressure for an average retention time of 0.5 hours. An esterification reaction product generated in the third esterification reactor vessel was continuously supplied into a three-stage continuous polycondensation reactor so as to be polycondensed, was filtered with a filter obtained by sintering stainless steel fibers with a 95%-cut diameter of 20 μm , was extruded into water after ultrafiltration, and was cut into chips after being cooled, thereby obtaining PET chips with intrinsic viscosity of 0.60 dl/g (hereinafter, abbreviated as PET (I)). A lubricant content in the PET chips was 0.6% by mass.

[0079]

(Preparation of polyethylene terephthalate pellet (PET (II)))

Whereas, in the production of the PET (I) chips, PET chips with intrinsic viscosity of 0.62 dl/g, which did not contain any particle of calcium carbonate, silica or the like at all, was obtained (hereinafter, abbreviated as PET (II)).

[0080]

(Preparation of polyethylene terephthalate pellet (PET (III)))

PET chips were obtained similarly to those of PET (I) except for replacing the kind and the content of the particles of the PET (I) with 0.75% by mass of synthesized calcium carbonate having an average particle diameter of 0.9 μm , to which an ammonium salt of polyacrylic acid was attached by 1% by mass with respect to the calcium carbonate (hereinafter, abbreviated as PET (III)). A content of a lubricant in the PET chips was 0.75% by mass.

[0081]

(Production of laminated film X1)

After being dried, these PET chips were melt respectively at 285°C and 290°C by individual melt extruders; were subjected to two-stage filtration with a filter obtained by sintering stainless steel fibers with a 95%-cut diameter of 15 μm and a filter obtained by sintering stainless steel particles with a 95%-cut diameter of 15 μm ; were merged in a feed block; were laminated so

that the PET (I) might constitute a surface layer B (opposite side layer to release surface) and the PET (II) might constitute a surface layer A (release surface side layer); were extruded (casted) into sheets at speed of 45 m/minute; were adhered electrostatically on a casting drum at 30°C by electrostatic adhesion; and were cooled, thereby obtaining a unstretched polyethylene terephthalate sheet with intrinsic viscosity of 0.59 dl/g. A layer ratio was adjusted to be PET (I)/(II) = 60% by mass/40% by mass by calculation of discharge amounts of the respective extruders. Subsequently, this unstretched sheet was heated by an infrared heater, and then was stretched by 3.5 times in a machine direction by using speed difference between rolls at roll temperatures of 80°C. Thereafter, the stretched sheet was introduced to a tenter, and was stretched by 4.2 times in a transverse direction at 140°C. Subsequently, the stretched sheet was treated by heat at 210°C in a heat-fix zone. Thereafter, the heat-treated sheet was subjected to relax treatment at 170°C by 2.3% in the transverse direction, thereby obtaining a biaxially-stretched polyethylene terephthalate film X1 with a thickness of 31 μm . Sa of the surface layer A of the obtained film X1 was 2 nm, and Sa of the surface layer B thereof was 28 nm.

[0082]

(Production of laminated film X2)

A biaxially-stretched polyethylene terephthalate film X2 with a thickness of 25 μm was obtained not by changing a layer structure or stretching conditions from those of the laminated film X1, but by changing the speed of casting and adjusting a thickness thereby. Sa of a surface layer A of the obtained film X2 was 3 nm, and Sa of a surface layer B thereof was 29 nm.

[0083]

(Laminated film X3)

As a laminated film X3, A4100 (COSMOSHINE (Registered Trademark), produced by TOYOB0 CO., LTD.) with a thickness of 25 μm was used. A4100 has a structure of not substantially containing particles in the film, but being provided with a coat layer which contains particles on a surface layer B side by in-line coating. Sa of a surface layer A of the laminated film X3 was 1 nm, and Sa of a surface layer B thereof was 2 nm.

[0084]

(Laminated film X4)

As a laminated film X4, E5101 (TOYOB0 ESTER (Registered Trademark) film, produced by TOYOB0 CO., LTD.) with a thickness of 25 μm was used. E5101 has a structure of containing particles in the film. Sa of a surface layer A of the laminated film X4 was 24 nm, and Sa of a surface

layer B thereof was 24 nm.

[0085]

(Example 1)

Coating liquid having a below-described composition was applied onto a surface layer A of a laminated film X1 using a reverse gravure so that a film thickness of a release layer after being dried might be 50 nm, and then was dried at 140°C for 15 seconds, thereby obtaining a release film for production of an ultrathin ceramic green sheet. Ceramic slurry was applied onto the obtained release film, and a coating property, peelability, a transfer amount of a silicone component, pinholes, curls and the like were evaluated, so that favorable evaluation results were obtained.

Methylethylketone	49.45 Parts by Mass
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Toluene	49.45 Parts by Mass
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Melamine-based Compound	0.95 Parts by Mass
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(Full Ether-type Methylated Melamine, Solid Content of 100%, Produced by SANWA CHEMICAL CO., LTD., Product Name of MW-30M, Weight Average Polymerization Degree of 1.3)

Release Agent	0.05 Parts by Mass
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(Polydimethylsiloxane with One Terminal Carboxyl-Modified, X22-3710, Solid Content of 100%, Produced by Shin-Etsu Chemical Co., Ltd., Alkyl Group Intervening

between Dimethylsiloxane and Carboxyl Group.)

Acid Catalyst	0.10 Parts by
Mass	

(p-Toluenesulfonic Acid, Produced by Hitachi Chemical Co., Ltd., Product Name of DRYER (Registered Trademark) 900, Solid Content of 50%)

[0086]

(Example 2)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for using coating liquid which contained: full ether-type methylated melamine by a content of 0.98 parts by mass; and a release agent (X22-3710) by an adding amount of 0.02 parts by mass, as a replace of the coating liquid of Example 1.

[0087]

(Example 3)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for using coating liquid which contained: full ether-type methylated melamine by a content of 0.9 parts by mass; and a release agent (X22-3710) by an adding amount of 0.1 parts by mass, as a replace of the coating liquid of Example 1.

[0088]

(Example 4)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for using coating liquid which contained: full ether-type methylated melamine by a content of 0.8 parts by mass; and a release agent (X22-3710) by an adding amount of 0.2 parts by mass, as a replace of the coating liquid of Example 1.

[0089]

(Examples 5 to 8)

Release films for production of ultrathin ceramic green sheets were obtained similarly to Example 1, except for changing the film thickness of the release layer of Example 1 into film thicknesses described in Table 1.

[0090]

(Example 9)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for replacing the substrate film of Example 1 with a laminated film X2 with a film thickness of 25 μm .

[0091]

(Example 10)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for replacing the laminated film of Example 1 with a laminated film X3.

[0092]

(Example 11)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for changing the drying conditions of Example 1 into 90°C for 15 seconds.

[0093]

(Example 12)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for changing the drying conditions of Example 1 into 110°C for 15 seconds.

[0094]

(Example 13)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for using coating liquid which contained X22-3701E (polydimethylsiloxane with a side chain carboxyl-modified, produced by Shin-Etsu Chemical Co., Ltd.) as a replace of the release agent of Example 1.

[0095]

(Example 14)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for using coating liquid which contained X22-162C (polydimethylsiloxane with both terminals carboxyl-

modified, produced by Shin-Etsu Chemical Co., Ltd.) as a replace of the release agent of Example 1.

[0096]

(Example 15)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for using coating liquid which contained MW-30 (full ether-type methylated melamine, produced by SANWA CHEMICAL CO., LTD., weight average polymerization degree of 1.5) as a replace of the full ether-type methylated melamine of Example 1.

[0097]

(Example 16)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for using coating liquid which contained MS-21 (full ether-type methylated melamine, produced by SANWA CHEMICAL CO., LTD., weight average polymerization degree of 1.8) as a replace of the full ether-type methylated melamine of Example 1.

[0098]

(Example 17)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for using coating liquid which contained MX-730 (imino-type methylated melamine, solid content of 80%, produced by SANWA CHEMICAL CO., LTD., weight average polymerization

degree of 2.4) as a replace of the full ether-type methylated melamine of Example 1.

[0099]

(Comparative Example 1)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for using coating liquid which contained no release agent for the coating layer of Example 1. Peel force became high, because no release agent was contained.

[0100]

(Comparative Example 2)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for using a laminated film X4 (E5101-25 μm , produced by TOYOB0 CO., LTD.) instead of the laminated film X1. Both of a surface layer A and a surface layer B of E5101 contained particles, and respectively had Sa of 24 nm. Since surface roughness was high, pinholes were generated on the ceramic green sheet.

[0101]

(Comparative Example 3)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for using coating liquid with a below-described composition. In Comparative Example 3, in which a larger amount of the

release agent was added, and the melamine-based compound was contained by only 70% by mass with respect to the release layer, an PDMS amount transferred to the ceramic green sheet was higher.

Methylethylketone	49.45 Parts by Mass
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Toluene	49.45 Parts by Mass
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Melamine-based Compound	0.70 Parts by Mass
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(Full Ether-type Methylated Melamine, Solid Content of 100%, Produced by SANWA CHEMICAL CO., LTD., Product Name of MW-30M, Weight Average Polymerization Degree of 1.3)

Release Agent	0.30 Parts by Mass
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(Polydimethylsiloxane with One Terminal Carboxyl-Modified, X22-3710, Solid Content of 100%, Produced by Shin-Etsu Chemical Co., Ltd.)

Acid Catalyst	0.10 Parts by Mass
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(p-Toluenesulfonic Acid, Produced by Hitachi Chemical Co., Ltd., Product Name of DRYER (Registered Trademark) 900, Solid Content of 50%)

[0102]

(Comparative Example 4)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for using coating liquid with a below-described composition.

BYK-370 is polydimethylsiloxane having two kinds of functional groups (an ester group and a hydroxyl group) in one molecule. Although a PDMS transfer amount was low and favorable, interaction between the hydroxyl group and a melamine-based compound was strong, and PDMS might not arise from the surface, whereby peel force became high.

Methylethylketone	48.38 Parts by Mass
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Toluene	48.37 Parts by Mass
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Melamine	0.95 Parts by Mass
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(Full Ether-type Methylated Melamine, Solid Content of 100%, Produced by SANWA CHEMICAL CO., LTD., Product Name of MW-30M, Weight Average Polymerization Degree of 1.3)

Release Agent	0.20 Parts by Mass
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(Polyester-Modified Polydimethylsiloxane Containing OH Group, BYK-370, Solid Content of 25%, Produced by BYK Japan KK)

Acid Catalyst	0.10 Parts by Mass
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(p-Toluenesulfonic Acid, Produced by Hitachi Chemical Co., Ltd., Product Name of DRYER (Registered Trademark) 900, Solid Content of 50%)

[0103]

(Comparative Example 5)

A release film for production of an ultrathin ceramic

green sheet was obtained similarly to Example 1, except for using coating liquid which contained polydimethylsiloxane with one terminal epoxy-modified (X22-173DX, produced by Shin-Etsu Chemical Co., Ltd.) as a replace of the release agent of Example 1. Since interaction between a melamine-based compound and an epoxy group might be weak, a PDMS transfer amount was higher.

[0104]

(Comparative Example 6)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for using coating liquid which contained polydimethylsiloxane with one terminal hydroxy-modified (X22-170DX, produced by Shin-Etsu Chemical Co., Ltd.) as a replace of the release agent of Example 1. Although PDMS transfer amount was low and favorable, interaction between a carbinol group and a melamine-based compound was strong, and PDMS might not arise from the surface, whereby peel force became high.

[0105]

(Comparative Example 7)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for using coating liquid with a below-described composition. Although a PDMS transfer amount was low and favorable, interaction between a hydroxyl group and a melamine-based

compound was strong, and PDMS might not arise from the surface, whereby peel force became high.

Methylethylketone	49.32 Parts by Mass
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Toluene	49.32 Parts by Mass
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Melamine-based Compound	1.25 Parts by Mass
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(Imino-Type Methylated Melamine, Solid Content of 80%, Produced by SANWA CHEMICAL CO., LTD., Product Name of MX-730, Weight Average Polymerization Degree of 2.4)

Release Agent	0.005 Parts by Mass
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(Polyether-Modified Polydimethylsiloxane Containing OH Group, BYK-377, Solid Content of 100%, Produced by BYK Japan KK)

Acid Catalyst	0.10 Parts by Mass
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(p-Toluenesulfonic Acid, Produced by Hitachi Chemical Co., Ltd., Product Name of DRYER (Registered Trademark) 900, Solid Content of 50%)

[0106]

(Comparative Example 8)

A release film for production of an ultrathin ceramic green sheet was obtained similarly to Example 1, except for using coating liquid with a below-described composition. Although a PDMS transfer amount was low and favorable, interaction between a hydroxyl group and a melamine-based

compound was strong, and PDMS might not arise from the surface, whereby peel force became high.

Methylethylketone	49.26 Parts by Mass
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Toluene	49.26 Parts by Mass
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Melamine-based Compound	1.18 Parts by Mass
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(Imino-Type Methylated Melamine, Solid Content of 80%, Produced by SANWA CHEMICAL CO., LTD., Product Name of MX-730, Weight Average Polymerization Degree of 2.4)

Release Agent	0.20 Parts by Mass
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(Polyester-Modified Polydimethylsiloxane Containing OH Group, BYK-370, Solid Content of 25%, Produced by BYK Japan KK)

Acid Catalyst	0.10 Parts by Mass
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(p-Toluenesulfonic Acid, Produced by Hitachi Chemical Co., Ltd., Product Name of DRYER (Registered Trademark) 900, Solid Content of 50%)

[0107]

[Table 1]

	Substrate Film				Release Layer												
	Type	Thickness (μm)	Surface Roughness (Sa)		Melamine		Release Agent		Acid Catalyst	Thickness of Release Layer (μm)	Drying Temperature ($^{\circ}\text{C}$)	Surface		Surface Free Energy			
			Surface Layer A	Surface Layer B	Type	Ratio in Release Layer (% by Mass)	Type	Ratio in Release Layer (% by Mass)	Type			Sa	P	γ_{sd}	γ_{sp}	γ_{sh}	γ_{s}
Example 1	X1	31	2	28	Full Ether-Type Methylated Melamine	95	Carboxyl-Modified PDMS	5	p-Toluenesulfonic Acid	0.05	140	2	38	21.9	1.3	0.4	23.6
Example 2	X1	31	2	28	Full Ether-Type Methylated Melamine	98	Carboxyl-Modified PDMS	2	p-Toluenesulfonic Acid	0.05	140	2	33	23.6	1.7	0.6	25.9
Example 3	X1	31	2	28	Full Ether-Type Methylated Melamine	90	Carboxyl-Modified PDMS	10	p-Toluenesulfonic Acid	0.05	140	3	44	21.8	1.3	0.4	23.5
Example 4	X1	31	2	28	Full Ether-Type Methylated Melamine	80	Carboxyl-Modified PDMS	20	p-Toluenesulfonic Acid	0.05	140	2	40	21.6	1.2	0.3	23.1
Example 5	X1	31	2	28	Full Ether-Type Methylated Melamine	95	Carboxyl-Modified PDMS	5	p-Toluenesulfonic Acid	0.1	140	3	32	21.9	1.2	0.3	23.4
Example 6	X1	31	2	28	Full Ether-Type Methylated Melamine	95	Carboxyl-Modified PDMS	5	p-Toluenesulfonic Acid	0.3	140	2	31	21.6	1.1	0.3	23
Example 7	X1	31	2	28	Full Ether-Type Methylated Melamine	95	Carboxyl-Modified PDMS	5	p-Toluenesulfonic Acid	0.5	140	2	29	21.5	1.2	0.4	23.1
Example 8	X1	31	2	28	Full Ether-Type Methylated Melamine	95	Carboxyl-Modified PDMS	5	p-Toluenesulfonic Acid	0.8	140	2	20	21.5	1.1	0.4	23
Example 9	X2	25	3	29	Full Ether-Type Methylated Melamine	95	Carboxyl-Modified PDMS	5	p-Toluenesulfonic Acid	0.05	140	3	42	21.8	1.3	0.4	23.5
Example 10	X3	25	1	2	Full Ether-Type Methylated Melamine	95	Carboxyl-Modified PDMS	5	p-Toluenesulfonic Acid	0.05	140	1	41	22.1	1.4	0.3	23.8
Example 11	X1	31	2	28	Full Ether-Type Methylated Melamine	95	Carboxyl-Modified PDMS	5	p-Toluenesulfonic Acid	0.05	90	2	38	22.5	1.4	0.4	24.3

[Table 1](continued)

Example 12	X1	31	2	28	Full Ether-Type Methylated Melamine	95	Carboxyl-Modified PDMS	5	p-Toluenesulfonic Acid	0.05	110	2	38	21.9	1.4	0.5	23.8
Example 13	X1	31	2	28	Full Ether-Type Methylated Melamine	95	Carboxyl-Modified PDMS	5	p-Toluenesulfonic Acid	0.05	140	2	38	21.4	1.1	0.3	22.8
Example 14	X1	31	2	28	Full Ether-Type Methylated Melamine	95	Carboxyl-Modified PDMS	5	p-Toluenesulfonic Acid	0.05	140	2	38	21.5	1.2	0.4	23.1
Example 15	X1	31	2	28	Full Ether-Type Methylated Melamine	95	Carboxyl-Modified PDMS	5	p-Toluenesulfonic Acid	0.05	140	2	37	24.3	1.2	0.3	25.8
Example 16	X1	31	2	28	Full Ether-Type Methylated Melamine	95	Carboxyl-Modified PDMS	5	p-Toluenesulfonic Acid	0.05	140	2	39	24.1	1.5	0.4	26
Example 17	X1	31	2	28	Imino-Type Methylated Melamine	95	Carboxyl-Modified PDMS	5	p-Toluenesulfonic Acid	0.05	140	2	43	24.2	1.4	0.6	26.2
Comparative Example 1	X1	31	2	29	Full Ether-Type Methylated Melamine	100	None	0	p-Toluenesulfonic Acid	0.05	140	3	47	30.3	4.9	1.2	36.4
Comparative Example 2	X4	25	24	24	Full Ether-Type Methylated Melamine	95	Carboxyl-Modified PDMS	5	p-Toluenesulfonic Acid	0.05	140	23	430	22.0	1.1	0.4	23.5
Comparative Example 3	X1	31	2	28	Full Ether-Type Methylated Melamine	70	Carboxyl-Modified PDMS	30	p-Toluenesulfonic Acid	0.05	140	2	29	21.6	1.1	0.3	23
Comparative Example 4	X1	31	2	28	Full Ether-Type Methylated Melamine	95	Polyester-Modified PDMS Containing OH Group	5	p-Toluenesulfonic Acid	0.05	140	2	28	27.0	4.5	0.8	32.3
Comparative Example 5	X1	31	2	28	Full Ether-Type Methylated Melamine	95	Epoxy-Modified PDMS	5	p-Toluenesulfonic Acid	0.05	140	2	45	25.3	1.9	0.1	27.3
Comparative Example 6	X1	31	2	28	Full Ether-Type Methylated Melamine	95	Carbinol-Modified PDMS	5	p-Toluenesulfonic Acid	0.05	140	2	29	15.5	13.8	0.8	30.1
Comparative Example 7	X1	31	2	28	Imino-Type Methylated Melamine	99.5	Polyether-Modified PDMS Containing OH Group	0.5	p-Toluenesulfonic Acid	1.2	140	2	36	27.1	3.2	0.8	31.1
Comparative Example 8	X1	31	2	28	Imino-Type Methylated Melamine	95	Polyester-Modified PDMS Containing OH Group	5	p-Toluenesulfonic Acid	0.05	140	2	63	29.1	4.6	0.8	34.5

PDMS: Polydimethylsiloxane

[0108]

[Table 2]

	Coating Property	Peel Force		Silicone Component Transfer Amount		Pinhole	Curl	
		(mN/mm ²)	Evaluation	Si (kcps)	Evaluation		Rising Quantity (mm)	Evaluation
Example 1	○	1.6	○	0.026	○	○	0.5	◎
Example 2	○	1.9	○	0.019	○	○	0.5	◎
Example 3	○	1.5	○	0.037	○	○	0.5	◎
Example 4	○	1.5	○	0.070	△	○	0.5	◎
Example 5	○	1.5	○	0.028	○	○	0.7	◎
Example 6	○	1.4	○	0.032	○	○	1.5	○
Example 7	○	1.5	○	0.039	○	○	3.1	△
Example 8	○	1.5	○	0.047	△	○	8.5	△
Example 9	○	1.6	○	0.026	○	○	0.5	◎
Example 10	○	1.6	○	0.026	○	○	0.5	◎
Example 11	○	2.2	△	0.031	○	○	0.2	◎
Example 12	○	1.6	○	0.028	○	○	0.4	◎
Example 13	○	2.1	△	0.029	○	○	0.5	◎
Example 14	○	2.1	△	0.030	○	○	0.5	◎
Example 15	○	1.7	○	0.030	○	○	0.5	◎
Example 16	○	1.8	○	0.032	○	○	0.5	◎
Example 17	○	2.4	△	0.035	○	○	0.5	◎
Comparative Example 1	○	6.4	×	0.000	○	×	0.5	◎
Comparative Example 2	○	1.8	○	0.026	○	×	0.5	◎
Comparative Example 3	○	1.8	○	0.150	×	○	0.3	◎
Comparative Example 4	○	2.8	×	0.023	○	△	0.5	◎
Comparative Example 5	○	1.4	○	0.226	×	○	0.5	◎
Comparative Example 6	○	2.6	×	0.025	○	△	0.5	◎
Comparative Example 7	○	3.1	×	0.020	○	△	10.3	×
Comparative Example 8	○	3.3	×	0.031	○	△	0.5	◎

INDUSTRIAL APPLICABILITY

[0109]

According to the present invention, a surface of a release layer is smooth, and an ultrathin ceramic green

sheet of 0.2 μm to 1.0 μm can be produced, which does not substantially generate defects such as pinholes onto the ceramic green sheet, and causes less transfer of polyorganosiloxane than a conventional release film for production of a ceramic green sheet.

CLAIMS

1. A release film for production of a ceramic green sheet, wherein

a biaxially-oriented polyester film is used as a substrate,

the substrate has a surface layer A which does not substantially contain inorganic particles on at least one surface of the substrate,

a release layer is laminated onto at least one surface of the surface layer A directly or via another layer,

the release layer is obtained by curing a composition containing at least a release agent and a melamine-based compound,

the release agent is polyorganosiloxane containing a carboxyl group, and

a content of the melamine-based compound is 80% by mass or more with respect to a solid content of the composition for forming the release layer.

2. The release film for production of a ceramic green sheet according to claim 1, comprising:

the surface layer A which does not substantially contain inorganic particles on the one surface of the

substrate; and

a surface layer B on a surface of the substrate opposite to the surface layer A,

wherein the surface layer B contains particles,

at least a part of the particles are silica particles and/or calcium carbonate particles, and

a total content of the particles with respect to a mass of the surface layer B is 5000 ppm to 15000 ppm.

3. The release film for production of a ceramic green sheet according to claim 1 or 2, wherein the release layer of the release film has an average area surface roughness (Sa) of 7 nm or less and a maximum protrusion height (P) of 100 nm or less.

4. A method for producing a ceramic green sheet, in which a ceramic green sheet is formed by using the release film for production of a ceramic green sheet according to any one of claims 1 to 3, wherein the formed ceramic green sheet has a thickness of 0.2 μ m to 1.0 μ m.

5. A method for producing a ceramic capacitor, which adopts the method for producing a ceramic green sheet according to claim 4.