

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 producing a ceramic green sheet, and, in more detail, relates to a release film for producing an ultrathin ceramic green sheet, which enables to produce an ultrathin ceramic green sheet with suppressed generation of process failures due to pinholes and thickness unevenness, while producing the ultrathin ceramic green sheet.

BACKGROUND ART

[0002]

Recently, according to the downsizing and capacity enlargement of multi-layered ceramic capacitors (abbreviated as MLCC), thickness reduction of ceramic green sheets have been required. Such a multi-layered ceramic capacitor can be produced by: forming a ceramic green sheet 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; printing electrodes to the obtained ceramic green sheet; subsequently peeling the

ceramic green sheet from the release film; laminating, pressing, degreasing and sintering the ceramic green sheets; and applying external electrodes to the ceramic green sheets.

[0003]

In order to increase a capacity of an MLCC having a small size, a thickness of a ceramic green sheet is required to be reduced, so that the film thickness thereof has been reduced to 1.0 μm or less, and further to 0.6 μm or less, and still further reduction in thickness has proceeded. However, there have been problems that, if reducing a thickness of a ceramic green sheet, defects such as pinholes and breaking are likely to be generated by extremely fine protrusions on a release film and force applied while peeling the ceramic green sheet from the release film.

[0004]

In order to solve these problems, as a release film to be used for forming a ceramic green sheet, a film obtained by providing a release layer on a polyester film and highly smoothening a surface of the release layer is proposed. Patent Document 1 discloses providing a smoothened layer on a surface of a polyester film and subsequently providing a release layer on the smoothened layer. Further, Patent Document 2 discloses forming a

release layer made of (meth)acrylic ester and a silicone-based component with a film thickness of 0.3 μm or more. According to the description of Patent Documents 1 and 2, it is disclosed that a surface of the release layer can have arithmetic average roughness Ra of 8 nm or less and a maximum protrusion height Rp of 50 nm or less.

[0005]

However, according to the technique disclosed in Patent Documents 1 and 2, since thicknesses of resin layers (the release layer and the smoothened layer) to be laminated onto the polyester film are large, it takes a long period of time to cure the resin layers, and an amount of organic solvent to be used is increased, thereby causing problems of heavy environmental load and the like. Also, the film thickness of the release layer is large, curls of an obtained release film have sometimes become a problem. Further, in the technique described in these documents, since an amount of a silicone-based component contained in the release layer is large, elastic modulus of the surface of the release layer becomes low, whereby there has been a concern that peeling becomes unstable.

[0006]

Further, as a release layer of the release film for forming a ceramic green sheet, following suggestion has been made. Patent Document 3 suggests a non-silicone-based

release layer which does not contain silicone. Patent Document 4 suggests a film in which a silicone resin is used for a release layer. However, if using a non-silicone-based release layer as the technique described in Patent Document 3, peeling force while peeling a ceramic green sheet becomes high, and a thinned ceramic green sheet may be damaged. Further, if using a release layer of a silicone-based resin as described in Patent Document 4, peel force while peeling a ceramic green sheet becomes low, but since a glass transition temperature of a silicone resin is generally a room temperature or lower, elastic modulus thereof becomes low, and the release layer is deformed during the peeling, thereby causing a problem that the peel force becomes unstable.

[0007]

Moreover, Patent Document 5 suggests a release layer containing an alkyd resin, an amino resin and a modified silicone resin. Further, Patent Document 6 suggests a release layer containing a melamine resin and polyorganosiloxane. It is suggested that, by mainly containing a crosslinked body such as a melamine resin as a binder for the release layer and adding a silicone-based resin as a release component, an elastic modulus of the release layer is increased, and both of deformability and peelability can be obtained.

[0008]

However, if the release layer contains a binder resin and a silicone-based resin as described in Patent Documents 5 and 6, since the binder resin and the silicone-based resin are greatly different in solubility into organic solvent, and surface tension of their solutions are greatly different, their compatibility is degraded during drying, and the respective resins are aggregated so as to generate protrusions, thereby causing a problem that surface roughness on the surface of the release layer is deteriorated. In the case of forming a ceramic green sheet with a thickness of 1.0 μm or less, or further of 0.6 μm or less, even this slight deterioration of the surface roughness leads to the generation of pinholes and the like, and thus increases a defect ratio of laminated ceramic capacitors to be obtained, whereby further smoothness has been sought.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0009]

Patent Document 1: JP-A-2014-177093

Patent Document 2: WO 2013/145864

Patent Document 3: JP-A-2010-144046

Patent Document 4: JP-A-2012-207126

Patent Document 5: JP-A-9-239913

Patent Document 6: JP-A-2017-7226

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0010]

In the light of the above-described problems, the present invention aims to provide a release film for producing a ceramic green sheet, in which even a release layer obtained by curing a composition containing at least a binder component and a silicone-based release agent can suppress deterioration of surface roughness due to aggregation of the above-described components during drying and have high smoothness, and which can obtain excellent peelability by adjusting an amount of the silicone-based component on a surface of the release layer.

MEANS FOR SOLVING THE PROBLEMS

[0011]

That is, the present invention includes following structures.

1. A release film for producing a ceramic green sheet, in which a polyester film is used as a substrate, the substrate has a surface layer A that does not substantially contain particles on at least one surface, and a release

layer is laminated onto the at least one surface of the surface layer A directly or via other layer, wherein the release layer is obtained by curing a composition that contains a binder component and a silicone-based release agent, an Si element ratio on a surface of the release layer is 2.0 at% or more and 10.0 at% or less, maximum protrusion height (P) on the surface of the release layer is 50 nm or less, and average area roughness (Sa) on the surface of the release layer is 1.5 nm or less.

2. The release film for producing a ceramic green sheet described above in 1, wherein the silicone-based release agent is a silicone-based resin having a polyether site or a carboxyl group.

3. The release film for producing a ceramic green sheet described above in 1 or 2, wherein a component derived from the silicone-based release agent is contained by 1 mg/m² to 15 mg/m² in the release layer.

4. The release film for producing a ceramic green sheet described above in any one of 1 to 3, wherein the binder component contains a resin that has a long-chain alkyl group and/or a silicone skeleton.

5. A method for producing a ceramic green sheet for forming a ceramic green sheet using the release film for producing a ceramic green sheet described above in any one of 1 to 4, wherein the formed ceramic green sheet has a

thickness of 0.2 μm to 1.0 μm .

6. A method for producing a ceramic capacitor, which adopts the method for producing a ceramic green sheet described above in 5.

EFFECT OF THE INVENTION

[0012]

The present invention can provide a release film for producing a ceramic green sheet, in which even a release layer that contains at least a binder component and a silicone-based release agent can suppress deterioration of surface roughness due to aggregation of the above-described components during drying and have high smoothness, and which has excellent peelability and can decrease defects such as pinholes even in production of the ultrathin ceramic green sheet with a film thickness of 0.2 μm to 1.0 μm having excellent peelability by adjusting an amount of a silicone-based component on a surface of the release layer.

MODE FOR CARRYING OUT THE INVENTION

[0013]

In order to solve the above-described problems, by keenly investigating and optimizing the drying conditions after applying the release layer and the content of the silicone-based compound in the release layer, the inventors

of the present invention have found that, when the release film for producing a ceramic green sheet, which is obtained by laminating a release layer onto at least one surface of a surface layer A of a polyester film having the surface layer A that does not substantially contain particles on the at least one surface, wherein the release layer is obtained by curing a composition that contains a binder component and a silicone-based release agent, maximum protrusion height (P) on the surface of the release layer is 50 nm or less, average area roughness (Sa) on the surface of the release layer is 1.5 nm or less, and an Si element ratio on an outermost surface of the release layer is 2.0 at% or more and 10.0 at% or less, forms the ultrathin ceramic green sheet with a film thickness of 0.2 μm to 1.0 μm , the ceramic green sheet can obtain excellent peelability and generate less defects such as pinholes. Hereinafter, the present invention will be described in detail.

[0014]

(Polyester Film)

Polyester which constitutes the polyester film to be used as a substrate in the present invention is not limited particularly, and film-formed 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 effects of the film of the present invention, known additives, for example, an antioxidant, a photostabilizer, an ultraviolet absorber, a crystallizer and the like may be added. The polyester film is preferably a biaxially-stretched polyester film because of its elastic modulus in both directions and the like.

[0015]

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.

[0016]

A method for producing the polyester film in the present invention is not limited particularly, and conventionally and generally used methods can be adopted. For example, the 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 un-stretched film; and stretching the un-stretched 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 un-stretched film is stretched in the vertical and transverse directions simultaneously.

[0017]

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 vertical and transverse directions preferably by once to 8 times and particularly preferably by twice to 6 times.

[0018]

A thickness of the polyester film is preferably 12 μm to 50 μm , is more preferably 15 μm to 38 μm , and is further 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 its use is not extremely large.

[0019]

The above-described biaxially-stretched 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 particles, on at least one surface thereof. 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 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 smoothness for winding the film into a roll shape, a coat layer containing particles and a binder is preferably provided onto the surface layer B.

[0020]

In the polyester film substrate of the present invention, it is preferable that the surface layer A constituting the surface to which the release layer is applied does not substantially contain particles. In this case, average area surface roughness (Sa) of the surface layer A is preferably 7 nm or less. Sa 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 (Sa) of the surface layer A is smaller,

but Sa 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 particles, and that the average area surface roughness (Sa) after laminating the coat layer satisfies the above-described range. In the present invention, "does not substantially contain particles" means that, in the case of, for example, inorganic particles, 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, unless positively adding the 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.

[0021]

In the 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 in the light of slipperiness and air releasability of the film, and in particular, preferably adopts silica particles and/or calcium carbonate particles. 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 (Sa) 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.

[0022]

As the particles to be contained in the surface layer B, other than the silica and/or calcium carbonate particles, inert inorganic particles and/or heat-resistant organic particles and the like can be used. The silica and/or calcium carbonate particles are more preferably used in the light of transparency and costs, but as the 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 the silica particles, porous colloidal silica is preferable, and in the case of using the 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.

[0023]

An average particle diameter of the particles to be added into the surface layer B is preferably 0.1 μm or more and 2.0 μm or less, and is particularly preferably 0.5 μm or more and 1.0 μm or less. The average particle diameter of the particles of 0.1 μm or more is preferable, because the slipperiness of the release film becomes favorable. Also, the average particle diameter of 2.0 μm or less is preferable, because pinholes are not likely to be generated to the ceramic green sheet due to the rough particles on the surface of the release layer.

[0024]

The surface layer B may contain two kinds or more of

particles which are made of different materials. Also, particles in the same kind with different particle diameters may be contained.

[0025]

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 coat 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.

[0026]

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.

[0027]

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.

[0028]

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.

[0029]

Moreover, in order to improve adhesiveness of the

release layer and the like 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 un-stretched or uniaxially-stretched film in the film formation process, and can also be subjected to corona treatment and the like. In the case of providing the coat layer onto the surface layer A, it is preferable that the coat layer does not substantially contain particles.

[0030]

(Release layer)

The release layer of the present invention is preferably obtained by curing a composition that contains at least a binder component and a silicone-based release agent. Within the range not losing the effects of the film of the present invention, other components than the resin or the compositions can also be added.

[0031]

(Binder component)

As the binder component to be contained in the composition for forming the release layer of the present invention is not limited particularly, but is preferably obtained by crosslinking a crosslinkable component to increase crosslink density of the release layer and improve durability, solvent resistance and the like of the release

layer. Thus, the binder component is preferably obtained by a reaction between a resin having a reactive functional group and a crosslinking agent. Also, it is preferable that either of the reactive functional group and the crosslinking agent is solely self-crosslinked. However, the present invention does not eliminate a form that the binder component is made only of the resin having the reactive functional group or the crosslinking agent.

[0032]

The resin having the reactive functional group is not limited particularly, but a polyester-based resin, a poly(meth)acrylic-based resin, a polyurethane-based resin, a polyolefin-based resin and the like can be suitably used. These resins preferably have at least one kind or more selected from a carboxyl group, a hydroxyl group, epoxy, an amino group and the like as the reactive functional group.

[0033]

The resin having the reactive functional group preferably has a long-chain alkyl group and/or a silicone skeleton as a part of a resin skeleton thereof. It is preferable to have a low surface free energy site such as a long-chain alkyl group and/or a silicone skeleton as a part of the resin skeleton, because below-described compatibility between the silicone-based release agent and the binder component becomes high, and aggregation is not

likely to occur during drying, thereby improving the smoothness.

[0034]

As specific examples of the resin containing the reactive functional group, which has a long-chain alkyl group in the resin skeleton, an alkyd resin, a (meth)acrylic resin and the like, each of which has a long-chain alkyl group as a side chain, can be exemplified. As the long-chain alkyl group to be used, a straight-chain alkyl group having a carbon number of 6 to 20 is suitable. It is preferable to have the above-described number of carbons, because surface free energy of the resin to be obtained can be decreased, and the compatibility with the silicone-based release agent can be improved.

[0035]

In the case of the alkyd resin having the long-chain alkyl group as the side chain, it can be obtained by mixing the acid having the long-chain alkyl group (for example, octylic acid, stearyl acid or the like) into polybasic acid such as phthalic acid, and mixing them with a polyhydric alcohol component (pentaerythritol, diethylene glycol or the like) so as to cause a dehydration condensation reaction.

[0036]

The (meth)acrylic resin having the long-chain alkyl

group as the side chain is preferably obtained by copolymerizing two kinds or more of (meth)acrylic monomers. As the monomer to be copolymerized, a monomer having a long-chain alkyl group (for example, lauryl (meth)acrylate, stearyl (meth)acrylate, isodecyl (meth)acrylate and the like) is preferably contained, and as a site of the reactive functional group, a monomer having a hydroxy group (for example, hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate and the like) is preferably contained. Besides the above-described monomers, other known monomer such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, hexanediol dimethacrylate and butanediol diacrylate can be contained to control Tg of the polymer to be obtained and provide a cross-linking property thereto, reactivity and the like.

[0037]

A content of the monomer having the long-chain alkyl group, which composes the obtained acrylic resin, is preferably 1 mol% or more and 50 mol% or less with respect to all monomers that compose the acrylic resin. The content of 1 mol% or more is preferable, because an effect of decreasing surface free energy can be obtained. The content of 50 mol% or less is preferable, because the monomer having the reactive functional group becomes relatively high, and crosslink density of the resin can be

high.

[0038]

As specific examples of the resin containing the reactive functional group which has the silicone skeleton in the resin skeleton, an alkyd resin, an acrylic resin and the like, each of which has a polydimethylsiloxane skeleton as the side chain, can be exemplified. As specific examples of their commercial products, SYMAC (Registered Trademark) US-350, US-352 (produced by TOAGOSEI CO., LTD., reactive functional group: carboxyl group), SYMAC (Registered Trademark) US-270 (produced by TOAGOSEI CO., LTD., reactive functional group: hydroxyl group) and the like can be exemplified.

[0039]

(Crosslinking agent)

It is also preferable that the binder component contains a crosslinking agent. The crosslinking agent is not limited particularly, but melamine-based, isocyanate-based, carbodiimide-based, oxazoline-based and epoxy-based crosslinking agents and the like can be used, and one kind or combination of two kinds or more may be used. In particular, a crosslinking agent that reacts with the reactive functional group introduced into the binder component is preferable.

[0040]

As the crosslinking agent to be used in the present invention, a melamine-based compound is preferable in the light of the reactivity. The use of the melamine-based compound is preferable, because even a thin film with an application amount of 0.2 g/m² or less after curing the release layer can be cured quickly, and crosslink density can be high.

[0041]

The melamine-based compound to be used in 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 triazine rings and methylol groups and/or alkoxymethyl groups respectively in one molecule. More specifically, an etherified compound and the like obtained by causing a dehydration condensation reaction of a methylol 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 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.

[0042]

As the melamine-based compound, hexamethylol melamine, hexamethoxy methylol melamine and the like, each of which has many crosslinking points in one molecule, are preferably used, because they can increase the crosslink density of the binder component. In the case of using an ether compound obtained by a dehydration condensation reaction of a methylol melamine derivative with alcohol, hexamethoxymethyl methylol melamine obtained by dehydration condensation with methyl alcohol is particularly preferable in the light of the reactivity.

[0043]

An amount of the crosslinking agent contained in the binder component of the present invention is preferably 15% by mass or more, is more preferably 30% by mass or more, and is further preferably 50% by mass with respect to the resin having the reactive functional group. Further, in the case where a resin film can be formed by self-condensation of the crosslinking agent, the binder component may be composed only of the crosslinking agent. Containing the crosslinking agent by 15% by mass or more is preferable, because the crosslink density of the release layer can be increased, and solvent resistance and an elastic modulus can be improved.

[0044]

(Catalyst)

The composition for forming the release layer of the present invention can also contain a catalyst to cure the crosslinking agent. In the case of using the melamine compound, an acid catalyst is preferably used, and carboxylic acid-based, metal salt-based, phosphate-based and sulfonic acid-based catalysts, which are not limited particularly, can be suitably used. Also, a block-type catalyst in which an acid site is blocked can be used. In particular, p-toluenesulfonic acid can be suitably used in the light of the reactivity. In the case of using the isocyanate-based compound, general catalysts can be used, and organic tin, an amine compound, a trialkylphosphine compound and the like can be suitably used.

[0045]

A content of the catalyst is preferably 0.1% by mass to 40% by mass with respect to the crosslinking agent contained in the composition for forming the release layer. More preferably, the content is 0.5% by mass to 30% by mass. Further preferably, the content is 0.5% by mass to 20% by mass. The content of 0.1% by mass or more is preferable, because a curing reaction is likely to proceed. Whereas, the content of 40% by mass or less is preferable, because the acid catalyst is not likely to be transferred to a ceramic green sheet to be formed, and bad influence is

not likely to be caused.

[0046]

(Silicone-based release agent)

The silicone-based release agent to be used for the release layer of the present invention is not limited particularly as far as it is a compound having a silicone structure in its molecule and within the range not losing the effects of the present invention, but

polyorganosiloxane and the like can be suitably used.

Among polyorganosiloxane, polydimethylsiloxane (abbreviated as PDMS) can be suitably used, and polydimethylsiloxane having a functional group as a part thereof is also preferable. Having a functional group is preferable, because intermolecular interaction such as a hydrogen bond with the binder resin is likely to be exhibited, and the silicone-based release agent is unlikely to transfer to the ceramic green sheet.

[0047]

The functional group to be introduced into the polydimethylsiloxane is not limited particularly, and may be either a reactive functional group or a nonreactive functional group. Further, the functional group may be introduced to one terminal of the polydimethylsiloxane, and may be introduced to both terminals or a side chain thereof. Moreover, a position(s) to be introduced may be

one or plural.

[0048]

As the reactive functional group to be introduced into the polydimethylsiloxane, an amino group, an epoxy group, a hydroxyl group, a mercapto group, a carboxyl group, a methacrylic group, an acrylic group and the like can be exemplified. As the nonreactive functional group, a polyether group, an aralkyl group, a fluoro alkyl group, a long-chain alkyl group, an ester group, an amide group, a phenyl group and the like can be used. Although not limited by theory, among the above-described functional groups, an epoxy group, a carboxyl group, a polyether group, a methacrylic group, an acrylic group and an ester group are preferable.

[0049]

The functional group to be introduced into the polydimethylsiloxane is more preferably a functional group that does not react with the binder component. For example, polydimethylsiloxane modified with a hydroxyl group or the like that reacts with a melamine resin reacts with melamine during the drying process, and thus is unlikely to be oriented to the surface of the release layer, and an Si element ratio on the surface of the release layer is decreased, whereby releasability may be hardly exhibited. Thus, an adding amount thereof is

necessary to be increased to provide the sufficient releasability, but in this case, the elastic modulus of the release layer may be decreased, whereby the release layer is likely to be deformed.

[0050]

The functional group to be introduced into the polydimethylsiloxane is preferably a functional group which does not react with the binder resin, is likely to be oriented to the surface of the release layer, and has small transferability to a ceramic green sheet because of the above-described reasons, in particular, a polyether group and an ester group are preferable, and a polyether group is particularly preferable. As the functional group which provides a relatively high Si element ratio on the surface of the release layer, even it reacts with the binder resin, a carboxyl group can be exemplified.

[0051]

The silicone-based release agent to be used in the present invention preferably has a molecular weight of 40000 or less. More preferably, its molecular weight is 30000 or less. The molecular weight of 40000 or less is preferable, because the silicone-based release agent is likely to be segregated to the surface of the release layer, thereby obtaining the favorable peelability.

[0052]

A content of the component derived from the silicone-based release agent, which is contained in the release layer after being cured in the present invention, is preferably 1 mg/m^2 or more and 15 mg/m^2 or less. The content thereof is further preferably 1 mg/m^2 or more and 10 mg/m^2 or less. The content of 1 mg/m^2 or more is preferable, because the silicone component can be deposited sufficiently to an outermost layer of the release layer, and the peelability of a ceramic green sheet can be stable. The content of 15 mg/m^2 or less is preferable, because an amount of the silicone component with a relatively low elastic modulus is small in the release layer, whereby the elastic modulus of the release layer does not become too low, and the peelability of a ceramic sheet can be stable. Herein, the silicone-based release agent may exist with its chemical structure unchanged even in the release layer after being cured, or may exist with its chemical structure changed by being chemically reacted with the binder component or the like. Then, as derived from the silicone-based release agent in the composition before being cured, a mass of a substance existing per unit area of the release layer after being cured is described as the content of the component derived from the silicone-based release agent. The content of the component derived from the silicone-based release agent can be obtained by calculating from a

present ratio (% by mass) of the silicone-based release agent in a solid content of the coating liquid containing the composition and an application amount (g/m^2) of the solid content of the release layer after being cured.

[0053]

The release layer of the present invention can contain particles and the like with a particle diameter of 1 μm or less, but does not preferably contain particles or the like which form protrusions, in the light of suppressing the generation of pinholes of a ceramic green sheet.

[0054]

Within the range not losing the effects 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 also preferably subjected to pretreatment such as anchor coating, corona treatment, plasma treatment and atmospheric plasma treatment, before being provided with a release-coated layer.

[0055]

The application amount of the release layer after being cured in the present invention is not limited particularly, but is preferably 1.0 g/m^2 or less. The

application amount thereof is more preferably 0.01 g/m² to 0.5 g/m², is further preferably 0.02 g/m² to 0.20 g/m², and is still more preferably 0.02 g/m² to 0.09 g/m². The application amount of the release layer of 0.01 g/m² or more is preferable, because a peeling function can be obtained. The application amount of the release layer of 0.2 g/m² or less is preferable, because a curing time of the release layer can be shorter, and flatness of the release film can be maintained, whereby thickness unevenness of a ceramic green sheet can be suppressed. Also, the application amount of 0.2 g/m² or less is preferable, because curls of the obtained film can be small, whereby forming accuracy can be improved while forming a ceramic green sheet.

[0056]

Surface free energy on the surface of the release layer of the release film of the present invention is preferably 18 mJ/m² or more and 35 mJ/m² or less. The surface free energy is more preferably 20 mJ/m² or more and 30 mJ/m² or less, and is further preferably 21 mJ/m² or more and 28 mJ/m² or less. The surface free energy of 18 mJ/m² or more is preferable, because cissing is unlikely to be generated while applying the ceramic slurry, whereby the ceramic slurry can be applied uniformly. Also, the surface free energy of 35 mJ/m² or less is preferable, because the

releasability of a ceramic green sheet is unlikely to be decreased. By setting the surface free energy within the above-described range, cissing is unlikely to be generated during the application, whereby the release film having excellent releasability can be provided.

[0057]

The release film of the present invention requires peel force while peeling a ceramic green sheet, which is preferably 0.5 mN/mm^2 or more and 3 mN/mm^2 or less. More preferably, the peel force is 0.8 mN/mm^2 or more and 2.5 mN/mm^2 or less. Further preferably, the peel force is 1.0 mN/mm^2 or more and 1.8 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 a ceramic green sheet is unlikely to be risen while it is conveyed. The peel force of 3 mN/mm^2 or less is preferable, because the ceramic green sheet is not likely to be damaged while it is peeled.

[0058]

The release film of the present invention generate less curls. Specifically, a curl of the film after being heated at 100°C for 15 minutes with no tension applied is preferably 2 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 2 mm or less is preferable, because, while forming a ceramic green

sheet and printing electrodes thereon, the curl can be small, and printing precision can be enhanced.

[0059]

It is preferable that, on the surface of the release layer of the release film of the present invention, the component derived from the silicone-based release agent contained in the release layer is deposited sufficiently. As an index that represents a deposition amount of the component derived from the silicone-based release agent, a ratio of an Si element on the surface of the release layer can be used. The Si element ratio on the surface of the release layer can be evaluated by an ESCA which can measure only the surface of the release layer. Incidentally, the Si element ratio of the present invention denotes a ratio (at%) of Si in five elements of C, S, Si, O and N as expressed by a following formula.

$$\text{Si Element Ratio (at\%)} = \{ \text{Si} / (\text{C} + \text{O} + \text{N} + \text{S} + \text{Si}) \} \times 100 \cdots \text{Formula}$$

[0060]

The Si element ratio on the outermost surface of the release layer of the release film of the present invention is preferably 2.0 at% or more. The Si element ratio thereon is more preferably 2.5 at% or more, is still more preferably 3.0 at% or more, and is further preferably 3.5 at% or more. The Si element ratio of 2.0 at% or more is

preferable, because the surface of the release layer can be coated sufficiently with the silicone-based release agent, whereby the peeling force can be stable while peeling a thin ceramic green sheet. An upper limit of the Si element ratio is preferably 10 at% or less, is further preferably 9 at% or less, and is still more preferably 8 at% or less. The upper limit of 10 at% or less is preferable, because the elastic modulus of the surface of the release layer does not become low, and the peeling can be stable.

[0061]

In order to attain the Si element ratio on the outermost surface of the release layer of the release film of the present invention, it is preferable to optimize: the above-described content of the component derived from the silicone-based release agent, which is contained in the release layer after being cured; and a below-described passing time of an initial drying process after applying the release layer.

[0062]

The surface of the release layer 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 average area surface roughness (S_a) on the surface of the release layer is preferably 1.5 nm or less, is further preferably 1.2 nm or

less, and is still further preferably 1.0 nm or less. Further, a maximum protrusion height (P) on the surface of the release layer is preferably 50 nm or less, is more preferably 40 nm or less, and is still more preferably 30 nm or less. It is preferable that the average area surface roughness (Sa) is 1.5 nm or less, and the maximum protrusion height (P) is 50 nm or less, because defects such as pinholes are not generated while forming a ceramic green sheet, thereby obtaining a favorable yield. It is more preferable as the average area surface roughness (Sa) is smaller, but may be 0.1 nm or more, and may also be 0.3 nm or more. It is also more preferable as the maximum protrusion height (P) is smaller, but may be 1 nm or more, and may also be 3 nm or more.

[0063]

Since the release film of the present invention adopts a substrate film that is highly flattened, the application amount of the release layer is preferably 0.2 g/m² or less, and if a thickness of the release layer is decreased to even less than 0.09 g/m², the surface of the release layer can be smooth, whereby amounts of solvents and resins to be used can be saved, and the release film for forming an ultrathin ceramic green sheet can be produced eco-friendly at low costs.

[0064]

In order to provide the maximum protrusion height (P) on the surface of the release layer of the release film of the present invention to be 50 nm or less and the average area roughness (Sa) thereof to be 1.5 nm or less, aggregation of the silicone-based release agent and the binder component is preferably suppressed until applying and drying the coating liquid of the release layer. Thus, by controlling a time after the application to the drying under a certain condition as described below in a producing method, the ultrasmooth surface of the release layer as is a target can be obtained.

[0065]

(Method for producing release film)

A method for producing the release film of the present invention is not limited particularly, but preferably adopts a method for laminating the release layer by: a coating process of lamination by applying the coating liquid, in which at least the binder component and the silicone-based release agent are dissolved or dispersed into a solvent, onto at least one surface of the polyester film as a substrate; an initial drying process for mainly removing the solvent and the like after the application; and a heat curing process for mainly curing the binder resin and the like. The surface to be provided with the release layer of the polyester film is preferably a surface

layer A which does not substantially contain particles, and other coat layer may be present between the surface layer A and the release layer.

[0066]

(Coating process)

The solvent for dissolving or dispersing the binder resin and the silicone-based release agent is not limited particularly, but an organic solvent is preferably used. The use of an organic solvent is preferable, because surface tension of the coating liquid can be decreased, cissing and the like are not likely to be generated after applying the coating liquid, whereby high smoothness on the surface of the release layer can be maintained.

[0067]

The organic solvent to be used in the method for producing the release film of the present invention is not limited particularly, and known organic solvents can be used. As the solvent, usually, aromatic hydrocarbon such as benzene, toluene and xylene, fatty acid hydrocarbon such as cyclohexane, n-hexane and n-heptane, halogenated hydrocarbon such as perchloroethylene, ethyl acetate, methylethylketone, methylisobutylketone and the like can be exemplified. Considering a coating property in the case of coating the surface of the substrate film, the practically preferable solvent is, but is not limited to, a mixed

solvent of toluene and methylethylketone.

[0068]

In the present invention, the coating liquid to be used for the application for forming the release layer preferably contain two kinds or more of organic solvents with different boiling points, which are not limited particularly. At least one kind of the organic solvent preferably has a boiling point of 100°C or more. By adding the solvent with a boiling point of 100°C or more, explosive boiling during the drying can be prevented, and the coating film can be levelled, whereby the smoothness on the surface of the coating film after being dried can be improved. An adding amount thereof is preferably about 10% by mass to about 50% by mass with respect to a total amount of the coating liquid. As the solvent with a boiling point of 100°C or more, toluene, xylene, octane, cyclohexanone, methylisobutylketone, n-propyl acetate and the like can be exemplified.

[0069]

In the present invention, surface tension (20°C) of the coating liquid while applying the coating liquid for forming 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 applying the coating liquid is improved, and unevenness on the surface

of the coating film after being dried can be reduced. In order to decrease the surface tension of the coating liquid, as the organic solvent for constituting the coating liquid, an organic solvent with low surface tension is preferably used. At least one kind of the organic solvent has surface tension (20°C) that is preferably 26 mN/m or less, and is further preferably 23 mN/m or less. Containing the organic solvent with surface tension (20°C) of 26 mN/m or less is preferable, because outer appearance defects such as cissing can be reduced during the application. An adding amount thereof is preferably 20% by mass or more with respect to the total amount of the coating liquid.

[0070]

Solid content concentration of the release agent contained in the coating liquid is preferably 0.1% by mass or more and 10% by mass or less, is more preferably 0.2% by mass or more and 8% by mass or less. The solid content concentration of 0.1% by mass or more is preferable, because the coating liquid can be dried quickly after the application, the components in the release agent are not likely to be aggregated. Whereas, the solid content concentration of 10% by mass or less is preferable, because viscosity of the coating liquid can be low, and a levelling property can be favorable, the flatness after the

application can be improved. The viscosity of the coating liquid is preferably 1 mPa·s or more and 100 mPa·s or less in terms of the coating outer appearance, and is more preferably 2 mPa·s or more and 10 mPa·s or less. The solid content concentration, the organic solvent and the like are preferably adjusted so that the viscosity may be within this range.

[0071]

In the present invention, the coating liquid for forming the release layer is preferably filtrated before the application. A filtration method is not limited particularly, and known methods can be adopted, but surface-type, depth-type and adsorption-type cartridge filters are preferably used. The use of a cartridge-type filter is preferable, because such a filter can be used while sending the coating liquid continuously from a tank to a coating part, and thus can filtrate the coating liquid efficiently with high productivity. As filtration accuracy of the filter, a filter which can remove substances in a size of 1 μm by 99% or more is preferably used, and a filter which can filtrate substances in a size of 0.5 μm by 99% or more is further preferably used. By using a filter with the above-described filtration accuracy, foreign substances mixed into the release agent can be removed, and foreign substances attached to the release film of the

release film for forming a ceramic green sheet of the present invention can be reduced significantly. Thus, defects of a ceramic green sheet formed by using the release film of the present invention can also be reduced, whereby a defect ratio of a ceramic capacitor can be lowered as well.

[0072]

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 a wire bar, die coating, spray coating, air knife coating and the like can be used.

[0073]

A film thickness (wet amount) of the coating liquid during the application is preferably 1 g/m² or more and 10 g/m² or less. The film thickness of more than 1 g/m² is preferable, because the application can be stable, and defects such as cissing and stripes are not likely to be generated. Further, the film thickness of 10 g/m² or less is preferable, because the coating liquid can be dried quickly, and the components contained in the release layer are not likely to be aggregated.

[0074]

(Drying process)

As a method for applying the coating liquid onto the substrate film and drying the coating liquid, well-known hot-air drying and heat drying by an infrared heater or the like can be exemplified, but hot-air drying with higher drying speed is preferable. A drying furnace can be divided for: a constant-rate drying process in initial drying (hereinafter called as an initial drying process); and a process of decreasing-rate drying and proceeding cure of the resin (hereinafter called as a heat curing process). The initial drying process and the heat curing process may be continuous or discontinuous, but are preferably continuous to obtain higher productivity. The respective processes are preferably discriminated by dividing the drying furnace into zones. The number of the zones for each process may be one or more.

[0075]

In the method for producing the release film of the present invention, the substrate film with the coating liquid applied is put into the drying furnace preferably within 1.5 seconds, more preferably within 1.0 second, and further preferably 0.8 seconds after the application. Putting the substrate film with the coating liquid into the drying furnace and starting drying within 1.5 seconds after the application is preferable, because the coating liquid can be dried before aggregating the components contained in

the release layer, thereby preventing deterioration of the smoothness on the surface of the release layer due to aggregation. It is preferable that the time after the application to the put into the drying furnace is shorter, and a lower limit thereof is not determined particularly, but the time may be 0.05 seconds or more, and may be 0.1 seconds or more.

[0076]

The initial drying process is not limited particularly, and a known drying furnace can be used. A system of the drying furnace may be either a roll support system or a floating system, but a roll support-system is preferable, because it can adjust air volume in a wider range during the drying, and can control air volume and the like according to the kind of the release layer.

[0077]

A temperature of the initial drying process is preferably 60°C or more and 140°C or less, is further preferably 70°C or more and 130°C or less, and is still further preferably 80°C or more and 120°C or less. The temperature of 60°C or more and 140°C or less is preferable, because an amount of the organic solvent contained in the release layer after the application can be dried effectively without generating flatness defects due to heat.

[0078]

A time for passing the initial drying process is preferably 1.0 second or more and 3.0 seconds or less, is more preferably 1.0 second or more and 2.5 seconds or less, and is further preferably 1.2 seconds or more and 2.5 seconds or less. The passing time of 1.0 second or more is preferable, because the organic solvent contained in the release layer after the application can be dried sufficiently. Further, the passing time of 1.0 second or more is preferable, because the component derived from the silicone-based release agent contained in the release layer can be deposited effectively to the surface of the release layer. Moreover, the passing time of 3.0 seconds or less is preferable, because the components in the release layer are not likely to be aggregated. By adjusting the solid content concentration, the kind of the organic solvent and the like so that the coating liquid can be dried within the above-described time period, the deterioration of the smoothness due to the aggregation can be suppressed, even if using the coating liquid that is easily aggregated.

[0079]

The amount of the organic solvent contained in the release layer after passing the initial drying process is preferably 5% by mass or less, and is more preferably 2% by mass or less. The amount of the organic solvent of 5% by

mass or less is preferable, because outer appearance deterioration due to explosive boil or the like can be prevented, even if it is heated in the heating process. The amount of the organic solvent in the release layer can be measured by gas chromatography, thermogravimetry or the like using the film which is sampled after the initial drying process, but a method of estimating the amount by simulation of drying can also be adopted. Obtaining the amount by such simulation is preferable, because the measurement can be carried out without stopping the process. The simulation is not limited particularly, but known simulation software can be used.

[0080]

(Heat curing process)

The release film of the present invention preferably undergoes the heat curing process after the initial drying process. The heat curing process is not limited particularly, and a known drying furnace can be used. A system of the drying furnace may be either a roll support system or a floating system. The heat curing process may be continuous or discontinuous to the initial drying process, but is preferably continuous in the light of the productivity.

[0081]

A temperature of the heat curing process is

preferably 80°C or more and 180°C or less, is more preferably 90°C or more and 160°C or less, and is most preferably 90°C or more and 140°C 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 generated. The temperature of 140°C or less is particularly preferable, because the film can be processed without losing its flatness, and thickness unevenness of a ceramic green sheet is further less likely to be generated. The temperature of 80°C or more is preferable, because curing can proceed sufficiently in the case of adopting a heat-curable resin.

[0082]

A passing time in the heat curing process is preferably 2 seconds or more and 30 seconds or less, and is further preferably 2 seconds or more and 20 seconds or less. The passing time of 2 seconds or more is preferable, because the curing of the heat-curable resin can proceed. Also, the passing time of 30 seconds or less is preferable, because the flatness of the film is not deteriorated by the heat.

[0083]

At an end of the heat curing process, a temperature of the hot air is preferably set at a glass transition temperature of the substrate film or less, and an actual

temperature of the substrate film in a state of being flat is preferably set at the glass transition temperature or less. In the case where the substrate film exits from the drying furnace while its actual temperature is the glass transition temperature or more, slipperiness becomes poor at the time when the substrate film gets in contact with a roll surface, whereby not only scratches but also curls and the like may be generated.

[0084]

The release film of the present invention is preferably wound into a roll shape after passing the heat curing process. A time after passing the heat curing process to the winding of the release film into a roll shape is preferably 2 seconds or more, and is further preferably 3 seconds or more. The time of 2 seconds or more is preferable, because the release film with its temperature increased in the heat curing process is cooled and then wound into a roll, whereby the flatness is not likely to be lost.

[0085]

According to the release film of the present invention and the method for producing the same, various treatment can be performed after the heat curing process until winding the release film into a roll shape, that is, aging treatment, destaticization treatment, corona

treatment, plasma treatment, ultraviolet irradiation treatment, electron beam irradiation treatment and the like can be performed.

[0086]

(Ceramic green sheet and ceramic capacitor)

Generally, a laminated ceramic capacitor has a rectangular parallelepiped 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 via the second end face.

[0087]

The release film for producing a 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 constituting the ceramic body is applied

to the release film of the present invention, which is used as a carrier film, and is dried. On the applied and dried ceramic green sheet, a conductive layer for constituting the first or second internal electrode is printed. The ceramic green sheet; the ceramic green sheet on which the conductive layer for constituting the first internal electrode is printed; and the ceramic green sheet on which the conductive layer for constituting 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 can be obtained. Thereafter, by forming the first and second external electrodes, a laminated ceramic capacitor can be produced completely.

EXAMPLES

[0088]

Hereinafter, the present invention will be described in further 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.

[0089]

(Average area surface roughness (Sa), maximum protrusion

height (P))

Surface roughness and protrusion heights are values obtained by measuring by using a noncontact surface shape measurement system (produced by Ryoka Systems Inc., 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
- Filter Treatment: Gaussian Cut-off Value of 50 μm

[0090]

(Application amount of release layer)

An application amount of the release layer of the release film of the present invention after being cured was measured by a gravimetric method. After sampling the

release film into a size of 15 cm × 15 cm and destaticizing the sampled release film by a static eliminator, its weight was measured by a precision balance (produced by Shimadzu Corporation, AUW120D). After wiping out the release layer of the weighed release film with methylethylketone, and drying it by a hot-air drier at 80°C for 1 minute, a mass of the film was measured by the precision balance again. By dividing a difference between the film weight before wiping out the release layer and the film weight after wiping out the release layer by the film area (15 cm × 15 cm), the application amount of the release layer (g/m²) was calculated. Incidentally, the measurement was carried out five times using the films which were sampled from different positions, and an average value of three measurement values obtained by eliminating a maximum value and a minimum value was used.

[0091]

(Si element ratio on outermost surface of release layer)

An Si element ratio on the outermost surface of the release layer of the release film of the present invention was measured by an ESCA. As the apparatus, K-Alpha+ (produced by Thermo Fisher Scientific Inc.) was used. Details of measurement conditions will be described below. By narrowly scanning the surface of the release layer about five elements of C, O, N, S and Si by this apparatus, the

Si element ratio (at%) was calculated by a below formula (in the present invention, the Si element ratio is determined as a ratio (at%) of Si in the five elements of C, O, N, S and Si).

Si Element Ratio (at%) = {Si/(C + O + N + S + Si)} × 100 ... Formula

Incidentally, in the analysis, a background was removed by Shirley method. Further, the surface Si element ratio was an average value of measurement results at three points or more.

Measurement Conditions

Excited X-ray: Monochromated Al Ka ray

X-ray output: 12 kV, 6 mA

Photoelectron Detachment Angle: 90°

Spot Size: 400 mm f (approximately)

Path Energy: 50 eV

Step: 0.1 eV

[0092]

(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 the

release surface of the 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, calculation software in this contact angle meter software (FAMAS) was used.

[0093]

(Surface tension of coating liquid)

Surface tension of the coating liquid was measured by Wilhelmy method using a surface tensiometer (produced by Kyowa Interface Science Co., Ltd.; high performance surface tensiometer, DY-500) and a platinum plate under a condition at 20°C. Measurement was carried out three times, and an average value thereof was adopted.

[0094]

(Viscosity of coating liquid)

Viscosity of the coating liquid was measured by a rotational viscometer (produced by TOKI SANGYO CO., LTD: TVB-15M) under conditions at 20°C. In the case of

measuring viscosity of liquid with low viscosity of 10 mPa·s or less, an optional low viscosity adapter was used for the measurement. Measurement was carried out three times, and an average value thereof was adopted.

[0095]

(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 60 minutes by using a bead mill, thereby obtaining ceramic slurry.

Toluene	76.3 Parts by Mass
Ethanol	76.3 Parts by Mass
Barium Titanate (Manufactured by FUJI TITANIUM INDUSTRY CO., LTD., HPBT-1)	35.0 Parts by Mass
Polyvinylbutyral (Manufactured by SEKISUI CHEMICAL CO., LTD., S-LEC (Registered Trademark) 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 μ m, and then was dried at 90°C for 1 minute, and a coating property was evaluated according to following criteria.

o: 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.

[0096]

(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 ceramic slurry was applied onto the release surface of the obtained release film sample by using an applicator so that the slurry after being dried might have a thickness of 1 μm , and then, after drying at 90°C for 1 minute, the release film was peeled off, thereby obtaining the ceramic green sheet.

Light was shed onto a range of 25 cm^2 in a central region along a film width direction 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.

[0097]

(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 (Manufactured by FUJI TITANIUM INDUSTRY CO., LTD., HPBT-1)	64.8 Parts by Mass
Polyvinylbutyral (Manufactured by SEKISUI CHEMICAL CO., LTD., S-LEC (Registered Trademark) 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 the 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 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.

[0098]

(Peeling stability evaluation of ceramic green sheet)

Similarly to the above-described peelability evaluation of the ceramic green sheet, evaluation on peelability was carried out ten times. Variation of ten values of peeling force was evaluated according to following criteria for the evaluation of the peeling stability.

○: A difference between a maximum value and a minimum value of the ten measurement values was less than 0.5 mN/mm^2 .

△: The difference between the maximum value and the minimum value of the ten measurement values was 0.5 mN/mm^2 or more and less than 1.0 mN/mm^2 .

×: The difference between the maximum value and the minimum value of the ten measurement values was less than 1.0 mN/mm^2 .

[0099]

(Curl evaluation of release film)

The release film sample was cut into a size of $10 \text{ cm} \times 10 \text{ cm}$, 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 a height of a part that rose from the glass plate was measured. Evaluation of the curling property was performed according to following criteria.

o: A height of a curl was 1 mm or less, and almost no curl was found.

△: A height of a curl was more than 1 mm and 2 mm or less, and the slight curl was found.

×: A height of curl was more than 2 mm.

[0100]

(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 trimethylphosphate (TMPA) 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 filtrated 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.

[0101]

(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)).

[0102]

(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. [0103]

(Production of laminated film X1)

After being dried, these PET chips were melt respectively at 285°C; were melt at 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 an un-stretched polyethylene terephthalate sheet with intrinsic viscosity of 0.59 dl/g. A layer ratio was adjusted to be PET (I)/PET (II) = 60%/40% by calculation of

discharge amounts of the respective extruders.

Subsequently, this un-stretched 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.

[0104]

(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.

[0105]

(Laminated film X3)

As a laminated film X3, A4100 (COSMOSHINE (Registered Trademark), produced by TOYOBO 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.

[0106]

(Laminated film X4)

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

[0107]

(Production of laminated film X5)

A biaxially-stretched polyethylene terephthalate film X5 with a thickness of 31 μm was obtained in a method similar to that of the laminated film X1 except for laminating the PET (III) as a surface layer B (opposite side layer to release surface) and the PET (II) as a surface layer A (release surface side layer) at a layer

ratio of PET (III)/(II) = 80%/20% by calculation of discharge amounts of the respective extruders. Sa of the surface layer A of the obtained film X5 was 2 nm, and Sa of the surface layer B thereof was 30 nm.

[0108]

(Resin Solution A) Long-chain Alkyl Group-Containing Acrylic Polyol

Stearyl (meth)acrylate by 20 mol%, hydroxyethyl (meth)acrylate by 40 mol% and methyl (meth)acrylate by 40 mol% were mixed, and were diluted with toluene so that solid content concentration might be 40% by mass, and 0.5 mol% of azobisisobutyronitrile was added under gas flow of nitrogen so as to be copolymerized therewith, thereby obtaining a resin solution A. At this time, weight average molecular weight of the obtained polymer was 30000.

[0109]

(Example 1)

After passing through a filter which can remove foreign substances of 0.5 μm or more by 99% or more, coating liquid 1 with a below-described composition was applied onto a surface layer A of a laminated film X1 using a reverse gravure so that an application thickness (wet amount) of the coating liquid 1 might be 5 g/m^2 , and then was prepared to enter an initial drying furnace after 0.5 seconds from the application. The coating liquid 1 was

dried at 100°C for 2 seconds in an initial drying furnace, and then was continuously heated at 130°C for 7 seconds in a heat curing process. After 8 seconds from the heat curing process, the film was wound into a roll shape, thereby obtaining a release film for producing an ultrathin ceramic green sheet. Results of measurement of a film thickness, surface roughness, surface free energy, curls and the like of the obtained release film were listed in Table 1. Further, ceramic slurry was applied onto the obtained release film, and a coating property, peelability and pinholes were evaluated, whereby favorable evaluation results were obtained.

(Coating Liquid 1) Solid Content of 1.0% by Mass, Surface Tension: 27 mN/m, Viscosity of 5 mPa·s

Methylethylketone	57.93 Parts by Mass
Toluene	40.00 Parts by Mass
Resin Solution A	1.75 Parts by Mass

(Long-chain Alkyl Group-Containing Acrylic Polyol, Solid Content of 40%)

Crosslinking Agent	0.25 Parts by Mass
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(Hexamethoxy Methylol Melamine, Solid Content of 100%)

Silicone-Based Release Agent	0.05 Parts by Mass
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(Polyether-Modified Polydimethylsiloxane, TSF4446, Solid Content of 100%, Manufactured by Momentive

Performance Materials Inc.)

Acid Catalyst (p-Toluenesulfonic Acid) 0.02 Parts
by Mass

[0110]

(Examples 2 to 4, Comparative Examples 1 and 7)

Release films for producing ultrathin ceramic green sheets were formed similarly to Example 1 except for changing the composition of the coating liquid 1 into ratios as listed in Table 1, respectively. The obtained release film was evaluated, whereby the release films of the examples which contain the silicone-based release agent provided excellent peelability and favorable results, but the release film of Comparative Example 1, which did not contain the silicone-based release agent, provided high peelability and results that defects such as pinholes were likely to be generated while peeling the ceramic green sheet from the release film. Also, the release film of Comparative Example 7, which had the small amount of the silicone-based release agent and the low Si element ratio on the surface of the release layer, provided low in-plane release uniformity.

[0111]

(Examples 5 to 7, Comparative Example 2)

Release films for producing ultrathin ceramic green sheets were formed similarly to Example 1 with the same

resin ratio of the coating liquid 1, except for changing the solid contents as listed in Table 2 and the application amounts (solid content) of the release layers, respectively.

As a result of evaluation of the obtained release films, curls were not found and favorable results were obtained in the examples in which the application amount of the release layer was 0.2 g/m² or less, but the results of largely deteriorated curls were obtained in Comparative Example 2, in which the application amount of the release layer was 0.75 g/m². Further, in Comparative Example 2, the content of the silicone-based release agent contained in the release layer was high, and the Si element ratio on the outermost surface of the release layer became high, so that the peeling stability tended to be deteriorated.

[0112]

(Example 8)

A release film for producing an ultrathin ceramic green sheet was formed similarly to Example 1 except for replacing the coating liquid 1 with coating liquid 8.

(Coating Liquid 8)

Methylethylketone	57.35 Parts by Mass
Toluene	40.00 Parts by Mass
SYMAC (Registered Trademark) US-270	2.33 Parts by Mass

(Silicone Group-Containing Acrylic Polyol,
Manufactured by TOAGOSEI CO., LTD., Solid Content of 30%)

Crosslinking Agent 0.25 Parts by Mass

(Hexamethoxy Methylol Melamine, Solid Content of
100%)

Silicone-Based Release Agent 0.05 Parts by Mass

(Polyether-Modified Polydimethylsiloxane, TSF4446,
Solid Content of 100%, Manufactured by Momentive
Performance Materials Inc.)

Acid Catalyst (p-Toluenesulfonic Acid) 0.02 Parts
by Mass

[0113]

(Example 9)

A release film for producing an ultrathin ceramic
green sheet was formed similarly to Example 1 except for
replacing the coating liquid 1 with coating liquid 9.

(Coating Liquid 9)

Methylethylketone 58.03 Parts by Mass

Toluene 40.00 Parts by Mass

Tesfine 305 1.90 Parts by Mass

(Long-Chain Alkyl Group-Containing Aminoalkyd Resin,
Manufactured by Hitachi Chemical Co., Ltd., Solid Content
of 50%)

Silicone-Based Release Agent 0.05 Parts by Mass

(Polyether-Modified Polydimethylsiloxane, TSF4446,

Solid Content of 100%, Manufactured by Momentive
Performance Materials Inc.)

Acid Catalyst (p-Toluenesulfonic Acid) 0.02 Parts
by Mass

[0114]

(Example 10)

A release film for producing an ultrathin ceramic
green sheet was formed similarly to Example 1 except for
replacing the coating liquid 1 with coating liquid 10.

(Coating Liquid 10)

Methylethylketone 57.55 Parts by Mass

Toluene 40.00 Parts by Mass

Tesfine 322 2.38 Parts by Mass

(Long-Chain Alkyl Group-Containing Aminoacrylic
Resin, Manufactured by Hitachi Chemical Co., Ltd., Solid
Content of 40%)

Silicone-Based Release Agent 0.05 Parts by Mass

(Polyether-Modified Polydimethylsiloxane, TSF4446,
Solid Content of 100%, Manufactured by Momentive
Performance Materials Inc.)

Acid Catalyst (p-Toluenesulfonic Acid) 0.02 Parts
by Mass

[0115]

(Example 11)

A release film for producing an ultrathin ceramic

green sheet was formed similarly to Example 1 except for replacing the coating liquid 1 with coating liquid 11, in which the resin solution A in the coating liquid 1 was replaced with 6AN-5000 (acrylic resin that does not contain a long-chain alkyl group) in the coating liquid 10.

(Coating Liquid 11)

Methylethylketone	57.93 Parts by Mass
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Toluene	40.00 Parts by Mass
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6AN-5000	1.75 Parts by Mass
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(Acrylic Polyol, Manufactured by TAISEI FINE CHEMICAL CO., LTD., Solid Content of 40%)

Crosslinking Agent	0.25 Parts by Mass
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(Hexamethoxy Methylol Melamine, Solid Content of 100%)

Silicone-Based Release Agent	0.05 Parts by Mass
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(Polyether-Modified Polydimethylsiloxane, TSF4446, Solid Content of 100%, Manufactured by Momentive Performance Materials Inc.)

Acid Catalyst (p-Toluenesulfonic Acid)	0.02 Parts by Mass
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[0116]

(Example 12)

A release film for producing an ultrathin ceramic green sheet was formed similarly to Example 1 except for replacing the coating liquid 1 with coating liquid 12.

(Coating Liquid 12)

Methylethylketone	58.95 Parts by Mass
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Toluene	40.00 Parts by Mass
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Hexamethoxy Methylol Melamine	0.95 Parts by Mass
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(Solid Content of 100%)

Silicone-Based Release Agent	0.05 Parts by Mass
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(Polyether-Modified Polydimethylsiloxane, TSF4446,

Solid Content of 100%, Manufactured by Momentive

Performance Materials Inc.)

Acid Catalyst (p-Toluenesulfonic Acid)	0.05 Parts by Mass
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[0117]

When the binder component was changed as Examples 8 to 12, favorable results were obtained. The resin containing a long-chain alkyl group or a silicone skeleton as the binder component tended to have lower surface protrusions, even if being processed in the same conditions.

[0118]

(Example 13)

A release film for producing an ultrathin ceramic green sheet was formed similarly to Example 1 except for replacing the coating liquid 1 with coating liquid 13.

(Coating Liquid 13)

Methylethylketone	57.78 Parts by Mass
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Toluene	40.00 Parts by Mass
Resin Solution A	1.75 Parts by Mass
(Long-Chain Alkyl Group-Containing Acrylic Polyol, Solid Content of 40%)	
Crosslinking Agent	0.25 Parts by Mass
(Hexamethoxy Methylol Melamine, Solid Content of 100%)	
Silicone-Based Release Agent	0.08 Parts by Mass
(Polyester-Modified Polydimethylsiloxane, BYK-310, Solid Content of 25%, Manufactured by BYK Japan KK)	
Acid Catalyst (p-Toluenesulfonic Acid)	0.02 Parts by Mass

[0119]

(Example 14)

A release film for producing an ultrathin ceramic green sheet was formed similarly to Example 1 except for replacing the coating liquid 1 with coating liquid 14.

(Coating Liquid 14)

Methylethylketone	57.93 Parts by Mass
Toluene	40.00 Parts by Mass
Resin Solution A	1.75 Parts by Mass
(Long-Chain Alkyl Group-Containing Acrylic Polyol, Solid Content of 40%)	
Crosslinking Agent	0.25 Parts by Mass
(Hexamethoxy Methylol Melamine, Solid Content of	

100%)

Silicone-Based Release Agent 0.02 Parts by Mass

(Carboxyl-Modified Polydimethylsiloxane, X22-3710,
Solid Content of 100%, Manufactured by Shin-Etsu Chemical
Co., Ltd.)

Acid Catalyst (p-Toluenesulfonic Acid) 0.02 Parts
by Mass

[0120]

(Example 15)

A release film for producing an ultrathin ceramic
green sheet was formed similarly to Example 1 except for
replacing the coating liquid 1 with coating liquid 15.

(Coating Liquid 15)

Methylethylketone 57.78 Parts by Mass

Toluene 40.00 Parts by Mass

Resin Solution A 1.75 Parts by Mass

(Long-Chain Alkyl Group-Containing Acrylic Polyol,
Solid Content of 40%)

Crosslinking Agent 0.25 Parts by Mass

(Hexamethoxy Methylol Melamine, Solid Content of
100%)

Silicone-Based Release Agent 0.08 Parts by Mass

(Polyester-Modified Hydroxyl Group-Containing
Polydimethylsiloxane, BYK-370, Solid Content of 25%,
Manufactured by BYK Japan KK)

Acid Catalyst (p-Toluenesulfonic Acid) 0.02 Parts
by Mass

[0121]

In either of Examples 13 to 15, which changed the kind of the silicone-based release agent, favorable results were obtained, but among them, the examples adopting the kinds which did not contain hydroxyl groups that react with the crosslinking agent (melamine in the present example) tended to result in the higher Si element ratio on the outermost surface of the release layer and the more favorable releasability in the same conditions.

[0122]

(Examples 16 to 18, Comparative Example 3)

Release films for producing ultrathin ceramic green sheets were formed similarly to Example 1 except for replacing the substrate film of Example 1 with respective substrate films listed in Table 1.

As a result of evaluation of the obtained release films, Sa and P on the surfaces of the release layers were low, and the pinhole evaluations were favorable in Examples 1 to 15 and 16 to 18 in which X1, X2, X3 and X5 containing no particle in the surface layer A of the substrate film were used respectively, but on the other hand, both of Sa and P on the surface of the release layer were high, and the pinhole evaluation was poor in Comparative Example 3 in

which X4 containing particles in the surface layer A of the substrate film and the application amount of the release layer was relatively small and thin.

[0123]

(Examples 19 to 22, Comparative Examples 4 and 5)

Release films for producing ultrathin ceramic green sheets were formed similarly to Example 1 except for changing the time from the application to entering the initial drying furnace, or the temperature of the initial furnace and the passing time as the producing conditions of Example 1 into conditions listed in Table 2.

[0124]

(Comparative Example 6)

A release film for producing an ultrathin ceramic green sheet was formed similarly to Example 11 except for changing the producing conditions of Example 11 into conditions listed in Table 1.

[0125]

(Comparative Example 8)

A release film for producing an ultrathin ceramic green sheet was formed similarly to Comparative Example 4 except for changing the content of the silicone-based release agent into a content listed in Table 1.

[0126]

As a result of evaluation of the obtained films, the

surface roughness Sa and the maximum protrusion height P on the surface of the release layer were low, and the pinhole evaluation was favorable in the examples in which the time from the application to entering the initial furnace was 1.5 seconds or less and the passing time in the initial drying furnace was 1.0 second or more and 3.0 seconds or less, and on the other hand, aggregation of the release layer was observed, and both of the surface roughness Sa and the maximum protrusion height P of the release layer were high in the comparative examples which were out of the above-described conditions. Further, in Comparative Examples 4 and 8 in which the passing time in the initial drying process was short, deposit of the silicone-based release agent on the surface of the release layer was small, and the Si element ratio on the outermost surface of the release layer tended to be low. Particularly in Comparative Example 8, the Si element ratio on the outermost surface of the release layer became low, and the peeling stability was deteriorated.

[0127]

[Table 1]

Composition for Forming Release Layer (Solid Content)									
Polyester Film	Binder Component					Silicone-Based Release Agent			
	Resin		Crosslinking Agent						
	Type	Ratio in Composition (% by mass)	Type	Ratio in Composition (% by mass)	Type	Ratio in Composition (% by mass)	Type	Ratio in Composition (% by mass)	Content in Release Layer (mg/m ²)
Example 1	X1	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25		Polyether-Modified PDMS	5	2.5
Example 2	X1	Acrylic Resin Having Long-Chain Alkyl Group	73	Hexamethoxy Methylol Melamine	25		Polyether-Modified PDMS	2	1
Example 3	X1	Acrylic Resin Having Long-Chain Alkyl Group	65	Hexamethoxy Methylol Melamine	25		Polyether-Modified PDMS	10	5
Example 4	X1	Acrylic Resin Having Long-Chain Alkyl Group	55	Hexamethoxy Methylol Melamine	25		Polyether-Modified PDMS	20	10
Example 5	X1	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25		Polyether-Modified PDMS	5	1
Example 6	X1	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25		Polyether-Modified PDMS	5	4.5
Example 7	X1	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25		Polyether-Modified PDMS	5	10
Example 8	X1	Acrylic Resin Containing Silicone Group	70	Hexamethoxy Methylol Melamine	25		Polyether-Modified PDMS	5	2.5
Example 9	X1	Aminoalkyd Resin Containing Long-Chain Alkyl Group	95	—	0		Polyether-Modified PDMS	5	2.5
Example 10	X1	Aminoacrylic Resin Containing Long-Chain Alkyl Group	95	—	0		Polyether-Modified PDMS	5	2.5
Example 11	X1	Acrylic Resin	70	Hexamethoxy Methylol Melamine	25		Polyether-Modified PDMS	5	2.5
Example 12	X1	—	—	Hexamethoxy Methylol Melamine	95		Polyether-Modified PDMS	5	2.5
Example 13	X1	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25		Ester-Modified PDMS	2	1
Example 14	X1	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25		Carboxyl-Modified PDMS	2	1
Example 15	X1	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25		Polyester-Modified OH Group-Containing PDMS	2	1

Example 16	X2	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25	Polyether-Modified PDMS	5	2.5
Example 17	X3	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25	Polyether-Modified PDMS	5	2.5
Example 18	X5	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25	Polyether-Modified PDMS	5	2.5
Example 19	X1	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25	Polyether-Modified PDMS	5	2.5
Example 20	X1	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25	Polyether-Modified PDMS	5	2.5
Example 21	X1	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25	Polyether-Modified PDMS	5	2.5
Example 22	X1	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25	Polyether-Modified PDMS	5	2.5
Comparative Example 1	X1	Acrylic Resin Having Long-Chain Alkyl Group	75	Hexamethoxy Methylol Melamine	25	—	—	—
Comparative Example 2	X1	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25	Polyether-Modified PDMS	5	37.5
Comparative Example 3	X4	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25	Polyether-Modified PDMS	5	2.5
Comparative Example 4	X1	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25	Polyether-Modified PDMS	5	2.5
Comparative Example 5	X1	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25	Polyether-Modified PDMS	5	2.5
Comparative Example 6	X1	Acrylic Resin	70	Hexamethoxy Methylol Melamine	25	Polyether-Modified PDMS	5	2.5
Comparative Example 7	X1	Acrylic Resin Having Long-Chain Alkyl Group	74	Hexamethoxy Methylol Melamine	25	Polyether-Modified PDMS	1	0.5
Comparative Example 8	X1	Acrylic Resin Having Long-Chain Alkyl Group	70	Hexamethoxy Methylol Melamine	25	Polyether-Modified PDMS	2	1

PDMS: Polydimethylsiloxane

[0128]

[Table 2]

	Coating Liquid			Condition for Production					
	Solid Content (% by mass)	Surface Tension (mN/m)	Viscosity (mPa•s)	Time from Application to Drying Furnace (s)	Initial Drying Process		Heat Curing Process		Time from Heating to Winding (s)
					Temperature (°C)	Passing Time (s)	Temperature (°C)	Passing Time (s)	
Example 1	1	27	5	0.5	100	2	130	7	8
Example 2	1	27	5	0.5	100	2	130	7	8
Example 3	1	27	5	0.5	100	2	130	7	8
Example 4	1	26	5	0.5	100	2	130	7	8
Example 5	0.4	27	4	0.5	100	2	130	7	8
Example 6	1.8	27	6	0.5	100	2	130	7	8
Example 7	4	28	7	0.5	100	2	130	7	8
Example 8	1	27	5	0.5	100	2	130	7	8
Example 9	1	27	5	0.5	100	2	130	7	8
Example 10	1	27	5	0.5	100	2	130	7	8
Example 11	1	27	5	0.5	100	2	130	7	8
Example 12	1	27	5	0.5	100	2	130	7	8
Example 13	1	27	5	0.5	100	2	130	7	8
Example 14	1	27	5	0.5	100	2	130	7	8
Example 15	1	27	5	0.5	100	2	130	7	8
Example 16	1	27	5	0.5	100	2	130	7	8
Example 17	1	27	5	0.5	100	2	130	7	8
Example 18	1	27	5	0.5	100	2	130	7	8
Example 19	1	27	5	0.8	100	2	130	7	8
Example 20	1	27	5	1.2	100	2	130	7	8
Example 21	1	27	5	0.5	100	1.5	130	7	8
Example 22	1	27	5	0.5	120	1.2	130	7	8
Comparative Example 1	1	29	5	0.5	100	2	130	7	8
Comparative Example 2	15	28	11	0.5	100	2	130	7	8
Comparative Example 3	1	27	5	0.5	100	2	130	7	8

Comparative Example 4	1	27	5	0.5	100	0.8	130	7	8
Comparative Example 5	1	27	5	1.7	100	2	130	7	8
Comparative Example 6	1	27	5	1.7	100	2	130	7	8
Comparative Example 7	1	28	5	0.5	100	2	130	7	8
Comparative Example 8	1	27	5	0.5	100	0.8	130	7	8

[0129]

[Table 3]

Properties of Release Film														
Application Amount of Release Layer (g/m²)	Average Area Surface Roughness Sa (nm)	Maximum Protrusion Height P (nm)	Surface Free Energy (mJ/m²)				Si Element Ratio (at%)		Peeling Force (mN/mm²)	Curl		Coating Property	Peeling Stability	Pinhole
			Ysd	Ysp	Ysh	Ys	Si	Height (mm)		Evaluation				
Example 1	0.05	1	36	20	4.4	0.9	25.3	4.5	1.3	Less Than 1	O	O	O	O
Example 2	0.05	0.9	33	20.4	4.5	1.1	26	2.5	1.3	Less Than 1	O	O	O	O
Example 3	0.05	1.1	36	18.6	4.9	0.8	24.3	6.7	1.3	Less Than 1	O	O	O	O
Example 4	0.05	1.2	39	18.1	4.3	0.9	23.3	9.3	1.1	Less Than 1	O	Δ	O	O
Example 5	0.02	0.9	30	21.2	4.6	0.8	26.6	2.9	1.3	Less Than 1	O	O	O	O
Example 6	0.09	1	37	19.9	4.3	0.9	25.1	7.1	1.3	Less Than 1	O	O	O	O
Example 7	0.2	1	36	18.7	4.3	0.8	23.8	8.6	1.2	1	Δ	O	O	O
Example 8	0.05	1	38	20.5	2.2	0.2	22.9	9.8	1.2	Less Than 1	O	Δ	O	O
Example 9	0.05	0.9	35	19.4	5.6	1	26	4.4	1.2	Less Than 1	O	O	O	O
Example 10	0.05	0.9	33	20	5.7	1	26.7	4.5	1.2	Less Than 1	O	O	O	O
Example 11	0.05	1.3	41	21	5.5	1.3	27.8	4.2	1.6	Less Than 1	O	O	O	Δ
Example 12	0.05	1.3	42	20.2	5.2	1.3	26.7	4.6	1.6	Less Than 1	O	O	O	Δ
Example 13	0.05	1	38	20.3	4.5	1.1	25.9	2.6	1.4	Less Than 1	O	O	O	O
Example 14	0.05	1	37	18.6	9	1.1	28.7	2.7	1.6	Less Than 1	O	O	O	O
Example 15	0.05	1	35	21.1	7.3	1.2	29.6	2	1.9	Less Than 1	O	O	Δ	Δ
Example 16	0.05	1.1	39	20.2	5	0.8	26	4.4	1.3	Less Than 1	O	O	O	O
Example 17	0.05	0.9	29	20.8	4.1	0.8	25.7	4.5	1.2	Less Than 1	O	O	O	O
Example 18	0.05	1	32	20.3	3.9	1.4	25.6	4.8	1.3	Less Than 1	O	O	O	O
Example 19	0.05	1.1	39	20.1	3.9	1.1	25.1	5.1	1.3	Less Than 1	O	O	O	O
Example 20	0.05	1.4	46	20	4.1	1.2	25.3	5.4	1.3	Less Than 1	O	O	O	O
Example 21	0.05	1	38	19.4	5.1	0.9	25.4	4	1.4	Less Than 1	O	O	O	O
Example 22	0.05	1.1	40	18.9	4.9	1.4	25.2	3.7	1.4	Less Than 1	O	O	O	O
Comparative Example 1	0.05	0.9	30	21.3	20.3	2.7	44.3	Less Than 0.1	3.5	Less Than 1	O	O	x	x
Comparative Example 2	0.75	1.1	39	19.5	3.9	0.9	24.3	15.8	1.4	5	x	Δ	x	O
Comparative Example 3	0.05	25	732	20.1	4.6	0.8	25.5	4.4	1.4	Less Than 1	O	O	O	x

Comparative Example 4	0.05	1.7	69	20.1	5.6	0.9	26.6	2.4	1.5	less than 1	O	O	Δ	X
Comparative Example 5	0.05	1.6	56	21	4.2	1.2	26.4	5.2	1.4	less than 1	O	O	O	X
Comparative Example 6	0.05	1.8	64	20.5	5.1	1.4	27	5.4	1.6	less than 1	O	O	O	X
Comparative Example 7	0.05	0.9	34	20.5	5.1	1.1	26.7	1.6	1.4	less than 1	O	O	X	O
Comparative Example 8	0.05	1.8	67	20.3	5.6	0.9	26.8	1.7	1.5	less than 1	O	O	X	X

INDUSTRIAL APPLICABILITY

[0130]

According to the present invention, by adopting a cured composition containing at least a binder component and a silicone-based release agent as a release layer of a release film for producing a ceramic green sheet, the release film which can suppress deterioration of surface roughness due to aggregation of the above-described components while being dried, has high smoothness, and exhibits excellent peelability can be provided. According to the present invention, even in production of an ultrathin ceramic green sheet with a film thickness of 0.2 μm to 1.0 μm , excellent peelability can be obtained, and defects such as pinholes of the ceramic green sheet can be reduced.

CLAIMS

1. A release film for producing a ceramic green sheet, in which a polyester film is used as a substrate, the substrate has a surface layer A that does not substantially contain particles on at least one surface, and a release layer is laminated onto the at least one surface of the surface layer A directly or via other layer, wherein

the release layer is obtained by curing a composition that contains a binder component and a silicone-based release agent, an Si element ratio on a surface of the release layer is 2.0 at% or more and 10.0 at% or less, maximum protrusion height (P) on the surface of the release layer is 50 nm or less, and average area roughness (Sa) on the surface of the release layer is 1.5 nm or less.

2. The release film for producing a ceramic green sheet according to claim 1, wherein the silicone-based release agent is a silicone-based resin having a polyether site or a carboxyl group.

3. The release film for producing a ceramic green sheet according to claim 1 or 2, wherein a component derived from the silicone-based release agent is contained

by 1 mg/m² to 15 mg/m² in the release layer.

4. The release film for producing a ceramic green sheet according to any one of claims 1 to 3, wherein the binder component contains a resin that has a long-chain alkyl group and/or a silicone skeleton.

5. A method for producing a ceramic green sheet for forming a ceramic green sheet using the release film for producing a ceramic green sheet according to any one of claims 1 to 4, wherein the formed ceramic green sheet has a thickness of 0.2 μm to 1.0 μm .

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