

DESCRIPTION

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

TECHNICAL FIELD

[0001]

The present invention relates to a release film for production of a ceramic green sheet. More specifically, the present invention relates to a release film for producing a ceramic green sheet, which can achieve both good winding properties and prevention of pinholes and partial thickness variation and the like even when the ceramic green sheet is reduced in thickness.

BACKGROUND ART

[0002]

A conventional technique has been disclosed, in which the surface roughness of a surface (rear surface) of a substrate film opposite to a surface on which a release agent layer is provided is relatively highly kept to eliminate a problem of sticking (blocking) and the like of front and rear surfaces of a release film for production of a ceramic green sheet stored in a rolled state (see, for example, Patent Document 1). However, such a conventional technique has a problem that large protrusions cause

pinholes and partial thickness variation.

[0003]

In order to reduce the heights of the protrusions, a technique is disclosed, which fills the protrusions on the rear surface with a coating layer to prevent the pinholes and the partial thickness variation from occurring in the ceramic green sheet (see, for example, Patent Document 2). However, such a conventional technique has a problem that the heights of the protrusions are low, but the density of the protrusions is low, so that a pressure applied to the protrusions is large, which has a problem that the pinholes occur when the ceramic green sheet is further reduced in thickness.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0004]

Patent Document 1: JP-A-2003-203822

Patent Document 2: JP-A-2014-144636

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005]

The present invention has been made in view of the problems of the conventional technique. That is, an object

of the present invention is to produce an excellent release film for producing a ceramic green sheet, which can achieve both good winding properties and prevention of pinholes and partial thickness variation and the like even when the ceramic green sheet is reduced in thickness.

MEANS FOR SOLVING THE PROBLEMS

[0006]

As a result of intensive studies to achieve the above object, the present inventors have completed the present invention. That is, the present invention has the following configurations.

1. A release film for producing a ceramic green sheet, the release film comprising:

a polyester film substantially containing no inorganic particles as a substrate;

a release coating layer on one surface of the substrate; and

an easy-to-slip coating layer containing particles on another surface of the substrate,

wherein:

a film elastic modulus measured from a surface opposite to the substrate in the release coating layer by a nanoindentation test on the release coating layer is 2.0 GPa or more; and

the easy-to-slip coating layer has average area surface roughness (Sa) of 1 nm or more and 25 nm or less, a maximum protrusion height (P) of 60 nm or more and 500 nm or less, and an average length of a roughness curve element (RSm) of 10 μm or less.

2. The release film for producing a ceramic green sheet according to the above 1, wherein the release coating layer has average area surface roughness (Sa) of 5 nm or less and a maximum protrusion height (P) of 30 nm or less.

3. The release film for producing a ceramic green sheet according to the above 1 or 2, wherein the easy-to-slip coating layer has a thickness of 0.001 μm or more and 2 μm or less.

4. A method for producing a ceramic green sheet using the release film for producing a ceramic green sheet according to any one of the above 1 to 3.

5. The method for producing a ceramic green sheet according to the above 4, wherein the ceramic green sheet to be produced has a thickness of 0.2 μm to 2.0 μm .

6. A method for producing a ceramic capacitor,

wherein the method for producing a ceramic green sheet according to the above 4 or 5 is employed.

EFFECT OF THE INVENTION

[0007]

The present invention can provide a release film for producing a ceramic green sheet, which can achieve both good winding properties and prevention of pinholes and partial thickness variation and the like even when the ceramic green sheet is reduced in thickness.

MODE FOR CARRYING OUT THE INVENTION

[0008]

Hereinafter, the present invention will be described in detail.

A release film for production of a ceramic green sheet of the present invention (hereinafter sometimes simply referred to as release film) is a release film including a release coating layer on one surface of a biaxially-stretched polyester film as a substrate film, and a easy-to-slip coating layer containing particles on the other surface.

[0009]

(Substrate Film)

A film preferably used as a substrate in the present

invention is a film composed of a polyester resin, and preferably a polyester film mainly containing at least one selected from polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, and polyethylene naphthalate. The film may be a film composed of a polyester with which a third component monomer is copolymerized as a dicarboxylic acid component of the polyester or a part of a diol component. The polyester film is preferably a biaxially-stretched polyester film for reasons such as a high bidirectional elastic modulus.

[0010]

The polyester film may have a single layer or a multilayer. In each of the layers, the polyester resin can contain various additives as needed as long as a desired effect in the present invention is exhibited. Examples of the additives include an antioxidant, a light-resistant agent, an anti-gelling agent, an organic wetting agent, an anti-static agent, and an ultraviolet absorber.

[0011]

(Easy-to-slip Coating Layer)

The release film of the present invention includes a easy-to-slip coating layer on one surface of the polyester substrate film as described above. The easy-to-slip coating layer preferably contains at least a binder resin and particles.

[0012]

(Binder Resin in Easy-to-slip coating layer)

The binder resin constituting the easy-to-slip coating layer is not particularly limited. Specific examples of the polymer include a polyester resin, an acrylic resin, an urethane resin, a polyvinyl-based resin (polyvinyl alcohol and the like), polyalkylene glycol, polyalkyleneimine, methylcellulose, hydroxycellulose, and starches. Among these, it is preferable to use a polyester resin, an acrylic resin, or an urethane resin from the viewpoints of retention of particles and adhesion. An acrylic resin is particularly preferable when the hardness of the easy-to-slip coating layer is considered. Other preferable examples of the binder resin constituting the easy-to-slip coating layer on the polyester substrate film include a polyester resin and an urethane resin. The polyester resin is preferably a copolymerized polyester. The polyester resin may be modified with polyurethane. Examples of the urethane resin include a polycarbonate polyurethane resin. Furthermore, an acrylic resin, a polyester resin, and a polyurethane resin may be used in combination, and the other binder resins may be used in combination.

[0013]

(Cross-Linking Agent)

In the present invention, in order to form a cross-linked structure in the easy-to-slip coating layer, the easy-to-slip coating layer may be formed to contain a cross-linking agent. The easy-to-slip coating layer contains the cross-linking agent, which makes it possible to further improve the hardness of the easy-to-slip coating layer. Specific examples of the cross-linking agent include urea-based, epoxy-based, melamine-based, isocyanate-based, oxazoline-based, and carbodiimide-based cross-linking agents. The oxazoline-based and carbodiimide-based cross-linking agents are particularly preferable in that the cross-linking density can be improved. In order to promote a crosslinking reaction, a catalyst and the like can be appropriately used as needed.

[0014]

(Particles in Easy-to-slip Coating Layer)

The easy-to-slip coating layer preferably contains lubricant particles in order to impart slipperiness to the surface of the easy-to-slip coating layer. The particles may be inorganic particles or organic particles, and are not particularly limited. Examples thereof include (1) inorganic particles such as silica, kaolinite, talc, light calcium carbonate, heavy calcium carbonate, zeolite, alumina, barium sulfate, carbon black, zinc oxide, zinc sulfate, zinc carbonate, zirconium oxide, titanium dioxide,

satin white, aluminum silicate, diatomaceous earth, calcium silicate, aluminum hydroxide, hydrous halloysite, calcium carbonate, magnesium carbonate, calcium phosphate, hydroxide magnesium, and barium sulfate, and (2) acryl-based or methacryl-based, vinyl chloride-based, vinyl acetate-based, nylon, styrene/acryl-based, styrene/butadiene-based, polystyrene/acryl-based, polystyrene/isoprene-based, polystyrene/isoprene-based, methyl methacrylate/butyl methacrylate-based, melamine-based, polycarbonate-based, urea-based, epoxy-based, urethane-based, phenol-based, diallyl phthalate-based, and polyester-based organic particles. Silica is particularly preferably used in order to impart appropriate slipperiness to the coating layer.

[0015]

The average particle size of the particles is preferably 10 nm or more, more preferably 20 nm or more, and still more preferably 30 nm or more. If the average particle size of the particles is 10 nm or more, the particles are less likely to aggregate to allow the slipperiness to be secured, which is preferable.

[0016]

The average particle size of the particles is preferably 1000 nm or less, more preferably 800 nm or less, and still more preferably 600 nm or less. If the average

particle size of the particles is 1000 nm or less, the transparency is maintained, and the particles do not fall off, which is preferable.

[0017]

For example, the mixture of small particles having an average particle size of about 10 to 270 nm and large particles having an average particle size of about 300 to 1000 nm is also preferable in order to reduce an average length of a roughness curve element (RSm) to achieve both slipperiness and smoothness while keeping average area surface roughness (Sa) and a maximum protrusion height (P) to be described later small. Particularly preferably, small particles of 30 nm or more and 250 nm or less and large particles having an average particle size of 350 to 600 nm are used in combination. When small particles and large particles are mixed, the mass content rate of the small particles is preferably greater than the mass content rate of the large particles with respect to the entire solid content of the coating layer.

[0018]

In a method for measuring the average particle size of particles, the particles in the cross section of the processed film are observed with a transmission electron microscope or a scanning electron microscope, and the 100 particles that do not aggregate are observed. The average

value of the particle sizes of the particles is determined as the average particle size.

[0019]

The shapes of the particles are not particularly limited as long as they satisfy the object of the present invention, and spherical particles and non-spherical particles having an irregular shape can be used. The average particle size of the particles having an irregular shape can be calculated as an equivalent circle diameter. The equivalent circle diameter is a value obtained by dividing the area of the observed particle by π , calculating the square root, and doubling the value of the square root.

[0020]

The ratio of the particles to the total solid content of the easy-to-slip coating layer is preferably 50% by mass or less, more preferably 40% by mass or less, and still more preferably 30% by mass or less. If the ratio of the particles to the total solid content of the easy-to-slip coating layer is 50% by mass or less, the transparency is maintained, and the falling-off of the particles from the easy-to-slip coating layer does not significantly occur, which is preferable.

[0021]

The ratio of the particles to the total solid content

of the easy-to-slip coating layer is preferably 1% by mass or more, more preferably 1.5% by mass or more, and still more preferably 2% by mass or more. If the ratio of the particles to the total solid content of the easy-to-slip coating layer is 1% by mass or more, the slipperiness can be secured, which is preferable.

[0022]

As a method for measuring the content rate of particles contained in a easy-to-slip coating layer, for example, the following method can be used when the easy-to-slip coating layer contains an organic component resin and inorganic particles. First, a easy-to-slip coating layer provided on a processed film is extracted from the processed film using a solvent or the like, and dried to take out the easy-to-slip coating layer. Next, only an inorganic component can be obtained by applying heat to the obtained easy-to-slip coating layer and burning off an organic component contained in the easy-to-slip coating layer with heat. By measuring the weights of the obtained inorganic component and the easy-to-slip coating layer before burning off, the % by mass of the particles contained in the easy-to-slip coating layer can be measured. At this time, measurement can be performed with high accuracy by using a commercially available differential heat-thermogravimetric simultaneous

measurement device. The ratio of the particles in the total solid content of the easy-to-slip coating layer means the ratio of the total amount of multiple types of particles when the multiple types of particles exist.

[0023]

(Additive in Easy-to-slip Coating Layer)

In order to impart other functionality to the easy-to-slip coating layer, various additives may be contained in the easy-to-slip coating layer as long as the coating appearance is not impaired. Examples of the additives include a fluorescent dye, a fluorescent whitener, a plasticizer, an ultraviolet absorbent, a pigment disperser, a foam-restraining agent, an anti-foaming agent, and a preservative.

[0024]

The easy-to-slip coating layer may contain a surfactant for the purpose of improving leveling properties during coating, and defoaming the coating solution. The surfactant may be any of cationic, anionic, and nonionic surfactants and the like, but the surfactant is preferably a silicone-based, acetylene glycol-based, or fluorine-based surfactant. These surfactants are preferably contained in the coating layer as long as the abnormality of the coating appearance does not occur when the surfactants are excessively added.

[0025]

As the coating method, any of a so-called in-line coating method in which a coating solution is simultaneously coated when a polyester substrate film is formed and a so-called off-line coating method in which a polyester substrate film is formed, and a coating solution is then separately coated with a coater can be applied. The in-line coating method is more efficient, and more preferable.

[0026]

A method for coating the coating solution to a polyethylene terephthalate (hereinafter sometimes abbreviated as PET) film may be any known method. Examples thereof include reverse roll-coating, gravure coating, kiss coating, die coating, roll brushing, spray coating, air knife coating, wire bar coating, pipe doctor, impregnation coating, and curtain coating methods. The coating is attained by using these methods alone or in combination.

[0027]

In the present invention, examples of a method for providing an easy-to-slip coating layer on a polyester film include a method for coating a coating solution containing a solvent, particles, and a resin on a polyester film, and then drying the coating solution. Examples of the solvent include an organic solvent such as toluene, water, and a

mixed solvent of water and a water-soluble organic solvent, but preferred is water alone, or a so-called water-based solvent of water and a water-soluble organic solvent from the viewpoint of environmental issues.

[0028]

The solid content concentration of the easy-to-slip coating solution is preferably 0.5% by mass or more, and more preferably 1% by mass or more, depending on the type of the binder resin and the type of the solvent, and the like. The solid content concentration of the coating solution is preferably 35% by mass or less, and more preferably 20% by mass or less.

[0029]

A drying temperature after coating is also preferably 70°C or more, and preferably 250°C or less depending on the type of the binder resin, the type of the solvent, the presence or absence of the cross-linking agent, and the solid content concentration, and the like.

[0030]

(Production of Polyester Film)

In the present invention, a polyester film as a substrate film can be produced according to a general method for producing a polyester film. Examples thereof include a method for melting a polyester resin, stretching a non-oriented polyester extrusion-molded into a sheet

shape in a machine direction utilizing the speed difference of rolls at a temperature equal to or higher than a glass transition temperature, thereafter stretching the polyester sheet in a transverse direction by a tenter, and heat-treating the polyester sheet. Another examples thereof include a method for simultaneously performing biaxial stretching in machine and traverse directions in a tenter.

[0031]

In the present invention, the polyester film as the substrate film may be a uniaxially stretched film or a biaxially-stretched film, but the polyester film is preferably a biaxially-stretched film.

[0032]

The thickness of the polyester film substrate is preferably 5 μm or more, more preferably 10 μm or more, and still more preferably 15 μm or more. If the thickness is 5 μm or more, wrinkles are less likely to occur when the film is transported, which is preferable.

[0033]

The thickness of the polyester film substrate is preferably 50 μm or less, more preferably 45 μm or less, and still more preferably 40 μm or less. If the thickness is 40 μm or less, the cost per unit area is reduced, which is preferable.

[0034]

In the case of in-line coating, a coating solution may be coated on an un-stretched film before stretching in a machine direction or a coating solution may be coated on a uniaxially stretched film before stretching in a transverse direction after stretching in a machine direction. When the coating solution is coated before stretching in the machine direction, it is preferable to provide a drying step before roll stretching. When the coating solution is coated on the uniaxially stretched film before stretching in the transverse direction, a film heating step in the tenter can also serve as the drying step, so that it is not necessary to separately provide a drying step. The same applies to simultaneous biaxial stretching.

[0035]

The film thickness of the easy-to-slip coating layer is preferably 0.001 μm or more, more preferably 0.01 μm or more, still more preferably 0.02 μm or more, and particularly preferably 0.03 μm or more. If the film thickness of the coating layer is 0.001 μm or more, the film-forming properties of the coating film is maintained to provide a uniform coating film, which is preferable.

[0036]

The film thickness of the easy-to-slip coating layer is preferably 2 μm or less, more preferably 1 μm or less,

still more preferably 0.8 μm or less, and particularly preferably 0.5 μm or less. If the film thickness of the coating layer is 2 μm or less, there is no fear of blocking, which is preferable.

[0037]

A ceramic green sheet to be coated and molded on the release coating layer to be described later is wound into a roll shape together with the release film after coating and molding. At this time, the ceramic green sheet is wound in a state where the easy-to-slip coating layer of the release film is brought into contact with the surface of the ceramic green sheet. In order not to cause defects in the surface of the ceramic green sheet, the outer surface of the easy-to-slip coating layer (the surface of the easy-to-slip coating layer of the entire coating film not brought into contact with the polyester film) needs to be moderately flat. It is preferable that average area surface roughness (S_a) is 1 nm or more and 25 nm or less, and a maximum protrusion height (P) is 60 nm or more and 500 nm or less.

[0038]

If the average area surface roughness (S_a) of the outer surface of the easy-to-slip coating layer is 1 nm or more and the maximum protrusion height (P) is 60 nm or more, the easy-to-slip coating surface is not too smooth to

allow appropriate slipperiness to be maintained, which is preferable. If the average area surface roughness (Sa) is 25 nm or less, and the maximum protrusion height (P) is 500 nm or less, the easy-to-slip coating surface does not become too rough to prevent the defects of the ceramic green sheet due to the protrusions from occurring, which is preferable.

[0039]

In the present invention, it is preferable that the average area surface roughness (Sa) and the maximum protrusion height (P) are set within the above ranges, and an average length of a roughness curve element (RSm) is 10 μm or less. By controlling the average length of the roughness curve element (RSm) to 10 μm or less, the number of the protrusions per unit area increases. If the number of the protrusions increases, a pressure applied to each protrusion is dispersed and reduced, whereby the occurrence of the pinholes can be effectively suppressed, which is preferable. The average length of the roughness curve element (RSm) is more preferably 5 μm or less, and still more preferably 3 μm or less. However, the too small average length of the roughness curve element (RSm) is related to the excessive content of the particles in the easy-to-slip coating layer, and the like. In addition, the too small average length is related to an increase in the

average area surface roughness (Sa) and an increase in the maximum protrusion height (P). The average length of the roughness curve element (RSm) is preferably 0.1 μm or more, may be 0.5 μm or more, and may be 1 μm or more.

[0040]

In the present invention, in order to set the average length of the roughness curve element (RSm) within a predetermined range, the average particle size of the particles contained in the easy-to-slip coating layer is preferably 1000 nm or less. The average particle size is more preferably 800 nm or less, and more preferably 600 nm or less. If the particle size is 1000 nm or less, the distance between the particles does not become too large, and RSm is adjusted to a predetermined range, which is preferable.

[0041]

(Release Coating Layer)

The release coating layer of the present invention preferably contains at least a release agent and a binder component. The release coating layer of the present invention preferably has a higher cross-linking density in order to suppress the deformation of the release coating layer. By increasing the cross-linking density, the solvent resistance is improved to prevent the erosion of the release coating layer caused by the solvent when a

slurry is coated. The film elastic modulus of the release coating layer is also improved, whereby the deformation during peeling can also be reduced.

[0042]

The binder component contained in the release coating layer of the present invention is not particularly limited, but in order to increase the cross-linking density of the release coating layer, the component that can be cross-linked is preferably cross-linked. As the binder component, a thermosetting type resin and an ultraviolet curing type resin and the like can be used.

[0043]

The binder component contained in the release coating layer of the present invention preferably contains two or more reactive functional groups

in one molecule. The binder component has two or more functional groups to allow the cross-linking density to be increased, which is preferable.

[0044]

Suitable examples of the binder component of the thermosetting resin include a melamine-based compound. The use of the melamine-based compound can provide a release coating layer having a high cross-linking density, which is preferable.

[0045]

(Melamine-Based Compound)

The melamine-based resin used for the release coating layer of the present invention is not particularly limited, and general melamine-based resins can be used. It is preferable that the melamine-based resin is obtained by condensing melamine and formaldehyde, and has a triazine ring, and at least one methylol group and/or alkoxymethyl group in one molecule. Specifically, preferred is a compound obtained by subjecting a methylol melamine derivative obtained by condensing melamine and formaldehyde, and methyl alcohol, ethyl alcohol, isopropyl alcohol, or butyl alcohol or the like as a lower alcohol to a dehydration condensation reaction, for etherification. Examples of the methylolated melamine derivative include monomethylol melamine, dimethylol melamine, trimethylol melamine, tetramethylol melamine, pentamethylol melamine, and hexamethylol melamine. One or two or more of the methylolated melamine derivatives may be used.

[0046]

The release coating layer in the present invention preferably has a high crosslinking density and a high film elastic modulus in order to suppress the deformation of the release coating layer. Therefore, as the melamine-based resin used for the release coating layer, it is preferable to use hexamethylol melamine having many cross-linking

points in one molecule, and capable of increasing the cross-linking density of the release coating layer.

[0047]

As the melamine-based resin used for the release coating layer of the present invention, methylol melamine and its derivatives are preferable. When an ether compound obtained by subjecting the methylol melamine derivative to a dehydration condensation reaction using an alcohol is used, from the viewpoint of reactivity, hexamethoxymethylmelamine obtained by dehydration condensation using methyl alcohol is particularly preferable.

[0048]

When the melamine-based compound is used as the binder of the release coating layer of the present invention, it is preferable to add a catalyst in order to promote the cross-linking reaction of the melamine-based compound. The catalyst to be used is not particularly limited, but existing acid catalysts can be used, and carboxylic acid-based, metal salt-based, phosphate ester-based, and sulfonic acid-based catalysts can be suitably used. A block type catalyst in which an acid moiety is blocked can also be used.

[0049]

When a sulfonic acid-based acid catalyst is used as

the acid catalyst, for example, p-toluenesulfonic acid, xylenesulfonic acid, cumenesulfonic acid, dodecylbenzenesulfonic acid, dinonylnaphthalenesulfonic acid, and trifluoromethanesulfonic acid and the like can be suitably used. Paratoluenesulfonic acid can be particularly suitably used.

[0050]

When the carboxylic acid-based acid catalyst is used as the acid catalyst, for example, benzoic acid, acetic acid, formic acid, oxalic acid, propionic acid, and derivatives thereof and the like can be used. The carboxylic acid-based acid catalyst is known to have lower acidity and poorer reactivity than those of other catalyst such as a sulfonic acid-based catalyst, but in the present invention, the carboxylic acid-based acid catalyst can also be sufficiently used. The reaction of the carboxylic acid-based acid catalyst is slower than that of the sulfonic acid-based acid catalyst, whereby the release agent is likely to be segregated on the surface in a drying step. This allows the addition of a smaller amount of the release agent to exhibit an effect of releasability, which is preferable. In particular, 4-methylbenzoic acid or the like is inexpensive, easily obtainable, and immediately easily usable.

[0051]

The addition amount of the acid catalyst is preferably 0.1 to 10% by mass with respect to the melamine resin contained in the release coating layer. The addition amount is more preferably 0.5 to 8% by mass. The addition amount is still more preferably 0.5 to 5% by mass. If the addition amount is 0.1% by mass or more, the curing reaction is likely to proceed, which is preferable. Meanwhile, if the addition amount is 10% by mass or less, the acid catalyst may not migrate to the ceramic green sheet to be molded, and adverse effects may not be caused, which is preferable.

[0052]

Suitable examples of a binder component for an ultraviolet curable resin include a cationic curing type resin and a radical curing type resin. Examples of the cationic curing type resin include an epoxy-based compound, an ether-based compound, and an oxetane-based compound. As the radical curing type resin, an acrylate-based compound can be suitably used. When the release coating layer has a thin thickness of 1 μm or less in the case of the radical curing type resin, an oxygen inhibition reaction may not cause curing to sufficiently proceed. Therefore, the cationic curing type resin can be sufficiently cured even when the release coating layer has a thin film thickness of 1.5 μm or less. This can provide a release coating layer

having a high cross-linking density, which is preferable. Among the cationic curing type resins, an epoxy-based compound has high reactivity, which is preferable.

[0053]

(Epoxy-Based Compound)

The epoxy-based compound used for the release film of the present invention is not particularly limited, and examples thereof include the following compounds: a bisphenol A type epoxy compound obtained by reacting bisphenol A and epichlorohydrin in the presence of alkali, a bisphenol F type epoxy compound, and a bisphenol AD type epoxy compound. Examples of a novolak type epoxy compound include a phenol novolak type epoxy compound and a cresol novolak type epoxy compound. Another examples thereof include trisphenol methane triglycidyl ether type epoxy compounds, and their hydrogenated products and brominated products.

[0054]

Examples of an alicyclic epoxy compound include a compound obtained by oxidizing a double bond with peracetic acid or the like in a compound containing a cyclohexene ring. Specifically, the following compounds are exemplified: 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate, 3,4-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-

methylcyclohexanecarboxylate, bis(3,4-epoxycyclohexyl)adipate, bis(3,4-epoxycyclohexylmethyl)adipate, bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate, 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy)cyclohexanone-meta-dioxane, and bis(2,3-epoxycyclopentyl)ether. Specific examples of the commercially available products include CELLOXIDE 2021P, CELLOXIDE 2081, and CELLOXIDE 2000 (manufactured by Daicel Corporation).

[0055]

Another examples thereof include diglycidyl ether of 1,4-butanediol, diglycidyl ether of 1,6-hexandiol, triglycidyl ether of glycerin, triglycidyl ether of trimethylolpropane, diglycidyl ether of polyethylene glycol, diglycidyl ether of polypropylene glycol, and polyglycidyl ethers of long chain polyols containing polyoxyalkylene glycol having an alkylene group having carbon atoms of 2 to 9 (preferably 2 to 4) or polytetramethylene ether glycol or the like.

[0056]

Examples of a glycidyl ester type epoxy compound include diglycidyl ester phthalate, diglycidyl tetrahydrophthalate, diglycidyl hexahydrophthalate, diglycidyl-p-oxybenzoate, glycidyl ether-glycidyl ester of salicylic acid, dimer acid glycidyl ester, and their

hydrogenated products.

[0057]

Examples of a glycidylamine type epoxy resin include triglycidyl isocyanurate, a N,N'-diglycidyl derivative of cyclic alkylene urea, a N,N,O-triglycidyl derivative of p-aminophenol, a N,N,O-triglycidyl derivative of m-aminophenol, and their hydrogenated products.

[0058]

The epoxy compound used for the release coating layer of the present invention may be used alone or in combination of two or more thereof. Among these epoxy group-containing compounds, an alicyclic epoxy compound is particularly suitable, and a polyfunctional alicyclic epoxy resin having two or more functional groups in one molecule is more preferable.

[0059]

(Cationic Polymerization Initiator)

When a cationic curing resin is used for the release coating layer of the present invention, it is preferable to use a cationic polymerization initiator. Examples of the cationic polymerization initiator include onium salts such as an aryldiazonium salt, an arylodonium salt, an arylhalonium salt, and an arylsulfonium salt, and organometallic complexes such as an iron-allene complex, a titanocene complex, and an arylsilanol-aluminum complex.

These may be used alone or in combination of two or more thereof.

[0060]

Examples of the commercially available products include PCI-220 and PCI-620 (manufactured by Nippon Kayaku Co., Ltd.), UVI6990 (manufactured by Union Carbide Corporation), SP-150, SP-152, SP-170, and SP-172 (manufactured by Asahi Denka Co., Ltd.), Uvacures (registered trademark) 1590 and 1591 (manufactured by Daicel UCB Corporation), Sun-Aids (registered trademark) SI-110, SI-180, SI-100L, SI-80L, and SI60L (manufactured by Sanshin Chemical Industry Co., Ltd.).

[0061]

The addition amount of the cationic polymerization initiator is not particularly limited. For example, it is preferable to use about 0.1 to 20% by mass of the cationic polymerization initiator with respect to the cationic curing resin to be used.

[0062]

When the photocationic polymerization initiator is used as the cationic polymerization initiator, it is desirable to use the photocationic polymerization initiator together with a photosensitizer. Examples of the photosensitizer include a carbonyl compound, an organic sulfur compound, a persulfide, a redox-based compound, azo

and diazo compounds, a halogen compound, and a photoreductive dye. Specific examples of the photosensitizer include benzoin derivatives such as benzoin methyl ether, benzoin isopropyl ether, and α,α -dimethoxy- α -phenylacetophenone; benzophenone derivatives such as benzophenone, 2,4-dichlorobenzophenone, methyl o-benzoylbenzate, 4,4'-bis(dimethylamino)benzophenone, and 4,4'-bis(dimethylamino)benzophenone; thioxanthone derivatives such as 2-chlorothioxanthone and 2-isopropylthioxanthone; anthraquinone derivatives such as 2-chloroanthraquinone and 2-methylantraquinone; acridone derivatives such as N-methylacridone and N-butylacridone; and other compounds such as α,α -diethoxyacetophenone, benzyl, fluorenone, xanthone, an uranyl compound, and a halogen compound. However, the photosensitizer is not limited thereto. These may be used alone or in a mixture thereof. The photosensitizer is preferably added in an amount of about 0.1 to 20% by mass with respect to the cationic curable resin.

[0063]

(Acrylate-Based Compound)

As the acrylate-based compound used for the release coating layer of the present invention, it is preferable to use a polyfunctional (meth)acrylate monomer or (meth)acrylate oligomer. In particular, a trifunctional or

more (meth)acrylate monomer or (meth)acrylate oligomer is preferable. The trifunctional or more (meth)acrylate monomer or (meth)acrylate oligomer can provide an improved cross-linking density, high solvent resistance, and reduced deformation of the release coating layer, which is preferable. The acrylate-based compounds may be used alone or in combination of two or more thereof. When the acrylate-based compounds are used in combination, at least one of the acrylate-based compounds is preferably trifunctional or more.

[0064]

Examples of the polyfunctional (meth)acrylate monomer include trimethylolpropane tri(meth)acrylate, dipentaerythritol tri(meth)acrylate, dipentaerythritol tetra(meth)acrylate, propionic acid-modified dipentaerythritol tri(meth)acrylate, pentaerythritol tri(meth)acrylate, propylene oxide-modified trimethylolpropane tri(meth)acrylate, tris((meth)acryloxyethyl)isocyanurate, propionic acid-modified dipentaerythritol penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate, and caprolactone-modified dipentaerythritol hexa(meth)acrylate. These may be used alone or in combination of two or more thereof.

[0065]

Examples of the polyfunctional (meth)acrylate

oligomer include a polyester acrylate-based oligomer, an epoxy acrylate-based oligomer, an urethane acrylate-based oligomer, an polyether acrylate-based oligomer, a polybutadiene acrylate-based oligomer, and a silicone acrylate-based oligomer.

[0066]

(Photo-Radical Initiator)

When a radical polymerization-based resin is used for the release coating layer of the present invention, it is preferable to add a photo-radical polymerization initiator. Specific examples of the photo-radical polymerization initiator include benzophenone, acetophenone, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, benzoin benzoic acid, benzoin methyl benzoate, benzoin dimethyl ketal, 2,4-diethylthioxanthone, 1-hydroxycyclohexyl phenyl ketone, benzyl diphenyl sulfide, tetramethyl thiuram monosulfide, azobisisobutyronitrile, benzyl, dibenzyl, diacetyl, β -chloroanthraquinone, (2,4,6-trimethyl benzyl diphenyl)phosphine oxide, and 2-benzothiazole-N,N-diethyldithiocarbamate. In particular, preferable examples for excellent surface curability include 2-hydroxy-1-[4-[4-(2-hydroxy-2-methyl-propionyl)-benzil]-phenyl]-2-methyl-propane-1-one, 1-hydroxy-cyclohexyl-phenyl-ketone, 2-hydroxy-2-methyl-1-phenyl-propane-1-one, and 2-methyl-1-[4-

(methylthio)phenyl]-2-morpholinopropane-1-one. Among these, 2-hydroxy-2-methyl-1-phenyl-propane-1-one and 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1-one are particularly preferable. These may be used alone or in combination of two or more thereof.

[0067]

The addition amount of the photo-radical polymerization initiator is not particularly limited. For example, it is preferable to use about 0.1 to 20% by mass of the photo-radical polymerization initiator with respect to the radical-based curing resin to be used.

[0068]

The binder component contained in the release coating layer of the present invention is preferably contained in an amount of 85% by mass or more, more preferably 90% by mass or more, and still more preferably 95% by mass, with respect to the solid content of the entire release coating layer. The release coating layer contains the binder component in an amount of 85% by mass or more, whereby the release coating layer has a high crosslinking density and can have high solvent resistance and a high film elastic modulus. This can provide suppressed deformation of the release coating layer when the ceramic green sheet is peeled off. In the present invention, components other than the binder component and the release agent component

in the release coating layer, such as the residual solvent, the acid catalyst, the photo-cationic initiator, and the photo-radical initiator are volatile, or present in trace amounts. In the present invention, the solid content of the entire release coating layer refers to the sum of the solid contents of the binder component and the release agent.

[0069]

(Release Agent)

As the release agent used for the release coating layer in the present invention (additive for improving the releasability of the release coating layer), a silicone-based additive, and a non-silicone-based additive such as an olefin-based, long-chain alkyl-based, or fluorine-based additive, and the like can be used. It is preferable to use a silicone-based additive from the viewpoint of peelability.

[0070]

The silicone-based additive is a compound having a silicone skeleton in its molecule, and polyorganosiloxane or the like can be suitably used. An acrylic resin or alkyd resin having polyorganosiloxane in its side chain can also be used. Among the polyorganosiloxanes, polydimethylsiloxane (abbreviated as PDMS) can be suitably used, and polydimethylsiloxane partially having a

functional group is also preferable. The polydimethylsiloxane has the functional group, whereby an intermolecular interaction between a binder component and a hydrogen bond or the like is likely to be exhibited, to cause difficult transition of the component to the ceramic green sheet, which is preferable.

[0071]

The functional group introduced into polydimethylsiloxane is not particularly limited, and may be a reactive functional group or a non-reactive functional group. The functional group may be introduced into one terminal, both terminals, or a side chain of polydimethylsiloxane. The functional group may be introduced into one position or each of a plurality of positions. Although theoretical consideration cannot be provided, the functional group is introduced into one terminal to exhibit good peelability, which is preferable.

[0072]

Two or more kinds of functional groups introduced into polydimethylsiloxane may be contained in one molecule, but one functional group is preferable. One functional group is less likely to cause an increased intermolecular interaction with the melamine binder component more than necessary to be likely to be oriented to the surface of the release coating layer, which is preferable.

[0073]

As the reactive functional group introduced into polydimethylsiloxane, an amino group, an epoxy group, a hydroxy group, a mercapto group, a carboxyl group, a methacryloyl group, and an acryloyl group and the like can be used. As the non-reactive functional group, a polyether group, an aralkyl group, a fluoroalkyl group, a long chain alkyl group, an ester group, an amide group, and a phenyl group and the like can be used. Although the present invention is not particularly bound by any theory, an epoxy group, a carboxyl group, a polyether group, a methacryloyl group, an acryloyl group, or an ester group is preferable.

[0074]

An acrylic resin, a polyester resin, or an urethane resin or the like having polydimethylsiloxane in its side chain can be suitably used. Examples of a commercially available acrylic resin having a silicone skeleton in its side chain include Cymac (registered trademark) US350 and Cymac (registered trademark) US352 (manufactured by Toagosei Co., Ltd.), and 8BS-9000 (manufactured by Taisei Fine Chemical Co., Ltd.).

[0075]

The fluorine-based additive is not particularly limited, and existing fluorine-based additives can be used. For example, a fluorine-based additive having a perfluoro

group and a fluorine-based additive having a perfluoroether group can be suitably used. Examples of commercially available products include Megaface (registered trademark) (manufactured by DIC Corporation) and Optool (registered trademark) (manufactured by Daikin Industries).

[0076]

As the long-chain alkyl-based additive, a long-chain alkyl-modified resin can be used, and a long-chain alkyl-based additive having an alkyl group having about 8 to 20 carbon atoms in its side chain such as polyvinyl alcohol and an acrylic resin is preferable. A copolymer that is a polymer having a (meth)acrylic acid ester as a main repeating unit, and contains a long-chain alkyl group having 8 to 20 carbon atoms in a transesterified portion can also be suitably used. Examples of commercially available products include Pyroyl (registered trademark) 1010, Pyroyl (registered trademark) 1050, and Pyroyl (registered trademark) 1070 (Lion Specialty Chemicals, Inc.), and Tesfine (registered trademark) 305 and Tesfine (registered trademark) 314 (manufactured by Hitachi Chemical Co., Ltd.).

[0077]

The release coating layer of the present invention preferably contains a release agent in an amount of 0.1% by mass or more and 15% by mass or less with respect to the

solid content of the entire release coating layer. The amount is more preferably 0.5% by mass or more and 10% by mass or less, and still more preferably 0.5% by mass or more and 5% by mass or less. When the amount is 0.1% by mass or more, the releasability is improved to provide improved peelability of the ceramic green sheet, which is preferable. Meanwhile, if the amount of 15% by mass or less, the film elastic modulus of the entire release coating layer does not excessively decrease to be likely to cause deformation of the release coating layer when the ceramic green sheet is peeled off, which is preferable. At this time, the solid content of the entire release coating layer is the sum of the solid contents of the binder component and the release agent.

[0078]

The release coating layer of the present invention can contain particles having a particle size of 1 μm or less, but from the viewpoint of the occurrence of pinholes, it is preferable that the release coating layer does not contain components forming protrusions such as particles.

[0079]

In the release coating layer of the present invention, an additive such as an adhesion improver or an antistatic agent may be added as long as the effect of the present invention is not impaired. In order to improve the

adhesion to the substrate, it is also preferable that the surface of the polyester film is subjected to a pretreatment such as anchor coating, a corona treatment, a plasma treatment, or an atmospheric pressure plasma treatment before providing the release coating layer.

[0080]

In the present invention, the thickness of the release coating layer may be set according to the purpose of use, and is not particularly limited. The weight of the release coating layer after curing is preferably in a range of 0.01 to 1.5 μm , more preferably 0.1 to 1.2 μm , and still more preferably 0.5 to 1.1 μm . If the thickness of the release coating layer is 0.01 μm or more, peeling performance is obtained, which is preferable. If the thickness is 1.5 μm or less, a curing time can be shortened, and the flatness of the release film can be maintained to provide suppressed thickness unevenness of the ceramic green sheet, which is preferable. If the thickness of the release coating layer is smaller, curling is reduced when the release film is heated, whereby no traveling failure occurs in the process of molding and drying the ceramic green sheet, which is preferable.

[0081]

The curl of the release film of the present invention after heating at 100°C for 15 minutes without applying

tension is preferably 3 mm or less, and more preferably 1 mm or less. Of course, it is also preferable that the release film does not curl at all. The curl of 3 mm or less can provide the ceramic green sheet having good traveling performance during molding and drying, to allow printing accuracy when an electrode is printed to be improved, which is preferable.

[0082]

The film elastic modulus of the surface of the release coating layer of the release film of the present invention measured by a nanoindentation test is 2.0 GPa or more, and preferably 2.3 GPa or more. If the film elastic modulus of the surface of the release coating layer is 2.0 GPa or more, the release coating layer is less likely to be deformed, whereby the release coating layer is less likely to follow the ceramic green sheet when the ceramic green sheet is peeled off from the release coating layer. This allows the ceramic green sheet to be normally peeled off, which is preferable. Meanwhile, the upper limit of the film elastic modulus of the surface of the release coating layer is not particularly limited, but the upper limit is preferably 10.0 GPa or less, and more preferably 7.0 GPa or less from the viewpoint of appropriately maintaining adhesion between the release coating layer and the PET substrate.

[0083]

In the present description, the measurement of the film elastic modulus of the surface of the release coating layer is performed by a nanoindentation test under an atmosphere of 23°C. Specifically, the rear surface side of a release film substrate cut into a size of 10 mm × 10 mm is fixed on a glass plate adhered to an aluminum stage with a two-component-type epoxy adhesive, and the nanoindentation test is performed using a microhardness evaluation device.

[0084]

The surface free energy of the surface of the release coating layer of the release film of the present invention is preferably 18 mJ/m² or more and 40 mJ/m² or less. The surface free energy is more preferably 23 mJ/m² or more and 35 mJ/m² or less, and still more preferably 23 mJ/m² or more and 30 mJ/m² or less. If the surface free energy is 18 mJ/m² or more, cissing is less likely to occur when a ceramic slurry is coated, and the ceramic slurry can be uniformly coated, which is preferable. If the surface free energy is 40 mJ/m² or less, the releasability of the ceramic green sheet may not be deteriorated, which is preferable. The surface free energy is set to the range, whereby the release film having excellent releasability can be provided without causing cissing during coating.

[0085]

In the release film of the present invention, a peeling force when the ceramic green sheet is peeled off is preferably 0.5 mN/mm^2 or more, and more preferably 0.8 mN/mm^2 or more. If the peeling force is 0.5 mN/mm^2 or more, the peeling force is not too light, and the ceramic green sheet may not float during transportation, which is preferable. Meanwhile, the peeling force is preferably 3 mN/mm^2 or less, and more preferably 2.5 mN/mm^2 or less. When the peeling force is 3 mN/mm^2 or less, the ceramic green sheet is less likely to be damaged during peeling, which is preferable.

[0086]

In the present invention, the method for forming the release coating layer is not particularly limited, and the following method is used. A coating solution in which a releasable resin is dissolved or dispersed is spread on one surface of the polyester film of the substrate by coating and the like. A solvent and the like is removed by drying, followed by heat drying, or heat curing.

[0087]

In the present invention, when a thermosetting resin such as melamine is used as a binder in the release coating layer, a drying temperature during solvent drying and thermosetting is preferably 100°C or higher and 180°C or

lower, more preferably 110°C or higher and 160°C or lower, and most preferably 125°C or higher and 150°C or lower. A heating time is preferably 30 seconds or less, and more preferably 20 seconds or less. When the temperature is 180°C or lower, the flatness of the film is maintained to be less likely to cause the uneven thickness of the ceramic green sheet, which is preferable. When the temperature is 140°C or lower, the film can be processed without impairing the flatness of the film, to further reduce the possibility of causing the uneven thickness of the ceramic green sheet, which is particularly preferable. When the temperature is 100°C or higher, the curing reaction of the thermosetting resin sufficiently proceeds to provide an increased film elastic modulus of the release coating layer, which is preferable.

[0088]

When an active energy ray-curable resin such as epoxy or acrylate is used as a binder for the release coating layer in the present invention, the drying temperature for solvent drying is preferably 50°C or higher and 110°C or lower, and more preferably 60°C or higher and 100°C or lower. The drying time is preferably 30 seconds or less, and more preferably 20 seconds or less. Furthermore, the solvent is dried, and the active energy ray-curable resin is then irradiated with active energy rays to cause the

curing reaction to proceed. As the active energy rays used at this time, ultraviolet rays, electron beams, and X-rays and the like can be used, but ultraviolet rays are preferable, because they can be easily used. The amount of light of ultraviolet rays with which the active energy ray-curable resin is irradiated is preferably 30 to 300 mJ/cm², more preferably 30 to 200 mJ/cm², and still more preferably 30 to 80 mJ/cm². By setting the amount of light to 30 mJ/cm² or more, the curing of the resin sufficiently proceeds, and by setting the amount of light to 300 mJ/cm² or less, the speed during processing can be improved, whereby the release film can be economically prepared, which is preferable.

[0089]

When a radical reactive active energy ray-curable resin such as acrylate is particularly used as the binder for the release coating layer in the present invention, the radical reactive active energy ray-curable resin is preferably irradiated with the active energy rays under a nitrogen gas atmosphere. An oxygen concentration is reduced under a nitrogen gas atmosphere to cause the radical reaction to smoothly proceed, whereby the film elastic modulus of the release coating layer can be improved, which is preferable.

[0090]

In the present invention, the surface tension of the coating solution when the release coating layer is coated is not particularly limited, but it is preferably 30 mN/m or less. By setting the surface tension as described above, the wettability after coating is improved, which can provide reduced unevenness of the surface of the coating film after drying.

[0091]

In the present invention, the coating solution when the release coating layer is coated is not particularly limited, but it is preferable to add a solvent having a boiling point of 90°C or higher. The addition of a solvent having a boiling point of 90°C or higher makes it possible to prevent bumping during drying, to level the coating film, and to improve the smoothness of the surface of the coating film after drying. The addition amount thereof is preferably about 10 to 80% by mass with respect to the whole coating solution.

[0092]

As the coating method of the coating solution, any known coating methods can be applied. For example, conventionally known methods such as a roll coating method (such as a gravure coating method or a reverse coating method), a bar coating method (such as a wire bar), a die coating method, a spray coating method, and an air knife

coating method can be utilized.

[0093]

The outer surface of the film on which the release coating layer has been formed (the surface of the release coating layer of the entire coating film that is not brought into contact with the polyester film) is desirably flat so as not to cause defects in the ceramic green sheet coated and molded thereon. It is preferable that the average area surface roughness (Sa) is 5 nm or less, and the maximum protrusion height (P) is 30 nm or less. More preferably, the average area surface roughness is 5 nm or less, and the maximum protrusion height is 20 nm or less. If the area surface roughness is 5 nm or less, and the maximum protrusion height is 30 nm or less, the defects such as pinholes do not occur when the ceramic green sheet is formed, and the yield is good, which is preferable. It can be said that the average area surface roughness (Sa) is preferably smaller, but the average area surface roughness may be 0.1 nm or more, or 0.3 nm or more. It can be said that the maximum protrusion height (P) is also preferably smaller, but the maximum protrusion height may be 1 nm or more, or 3 nm or more.

[0094]

In the present invention, in order to adjust the surface of the film on which the release coating layer has

been formed to a predetermined roughness range, it is preferable that the PET film substantially contains no inorganic particles. In the present invention, "substantially containing no inorganic particles" means that, when both the substrate film and the release coating layer are quantitatively analyzed for elements derived from particles by fluorescent X-ray analysis, the amount of the elements is 50 ppm or less, preferably 10 ppm or less, and most preferably equal to or less than the detection limit. This is because, even if the particles are not actively added into the substrate film, contaminant components derived from foreign substances, raw material resins, or pollution adhering to lines or apparatuses in a film production process may be peeled off and mixed into the film.

[0095]

(Ceramic Green Sheet and Ceramic Capacitor)

In general, a multilayer ceramic capacitor includes a rectangular parallelepiped ceramic primary body. In the ceramic primary body, first internal electrodes and second internal electrodes are alternately provided along a thickness direction. The first internal electrode is exposed in a first end face of the ceramic primary body. A first external electrode is provided on the first end face. The first internal electrode is electrically connected to

the first external electrode in the first end face. The second internal electrode is exposed in a second end face of the ceramic primary body. A second external electrode is provided on the second end face. The second internal electrode is electrically connected to the second external electrode in the second end face.

[0096]

The release film for production of a ceramic green sheet of the present invention is used for production of such a multilayer ceramic capacitor. For example, the release film for production of a ceramic green sheet is produced as follows. First, the release film of the present invention is used as a carrier film, and a ceramic slurry for constituting a ceramic primary body is coated and dried. A conductive layer for constituting a first or second internal electrode is printed on the coated and dried ceramic green sheet. A ceramic green sheet, the ceramic green sheet printed with a conductive layer for constituting the first internal electrode, and the ceramic green sheet printed with a conductive layer for constituting the second internal electrode are appropriately laminated and pressed to obtain a mother laminated body. The mother laminated body is divided into a plurality of parts to prepare a raw ceramic primary body. The raw ceramic primary body is fired to obtain a ceramic

primary body. Thereafter, the multilayer ceramic capacitor can be completed by forming first and second external electrodes.

EXAMPLES

[0097]

Next, the present invention will be described in detail with reference to Examples and Comparative Examples, but the present invention is naturally not limited to the following Examples. Evaluation methods used in the present invention are as follows.

[0098]

(1) Surface Characteristics of Coating Film

The surface characteristics of the coating film are represented by values measured under the following conditions using a non-contact surface shape measurement system (VertScan R550H-M100). For average area surface roughness (Sa) and an average length of a roughness curve element (RSm), the average value of five measurements were employed. For a maximum protrusion height (P), the maximum value of five measurements was employed.

(Measurement Conditions)

- Measurement mode: WAVE mode
- Objective lens: 50x
- 0.5 × Tube lens

- Measurement area $187 \times 139 \mu\text{m}$ (Sa, P measurement)
- Measurement length (Lr: reference length): $187 \mu\text{m}$ (RSm measurement)

[0099]

(2) Evaluation of Pinholes and Thickness Variation of Ceramic Green Sheet

The compositions containing the following materials were stirred and mixed, and the mixture was dispersed for 2 hours using a paint shaker with 2.0 mm glass beads as a dispersion medium to obtain a ceramic slurry.

Toluene 22.5% by mass

Ethanol 22.5% by mass

Barium titanate (HPBT-1, manufactured by Fuji Titanium Industry Co., Ltd.) 50% by mass

Polyvinyl butyral 5% by mass
(S-LEC BH-3, manufactured by Sekisui Chemical Co., Ltd.)

Then, the slurry was coated on the release surface of the release film sample using an applicator such that the thickness after drying was $0.5 \mu\text{m}$, and dried at 90°C for 1 minute. Then, the surface of the slurry and the surface of the smoothed coating layer were overlaid. A load of 1 kg/cm^2 was applied for 10 minutes, and the release film was then peeled off to obtain a ceramic green sheet.

In the central region of the obtained ceramic green sheet in the film transverse direction, light was applied

from the opposite surface of the coating surface of the ceramic slurry in a range of 25 cm², and the occurrence status of pinholes viewed from the transmission of light was observed. The pinholes were visually determined according to the following criteria.

GOOD: No occurrence of pinholes, thickness variation is not particularly problematic

POOR: Pinholes slightly occur and/or thickness variation is slightly conspicuous.

VERY POOR: Less pinholes occur and thickness variation is slightly conspicuous.

EXTREMELY POOR: A large number of pinholes occur and thickness variation is largely conspicuous.

[0100]

(3) Evaluation of Film Elastic Modulus of Surface of Release Coating Layer

The release films obtained in each of Examples and Comparative Examples were cut into a size of 10 mm × 10 mm. The rear surface of the cut release film substrate was then fixed to a glass plate adhered to an aluminum stage using a two-component-type epoxy adhesive. A nanoindentation test was performed using a microhardness evaluation device (ENT-3100, manufactured by ELIONIX INC.) under a condition of a maximum indenting depth of an indenter of 50 nm and an atmosphere of 23°C, to measure the film elastic modulus of

the release coating layer of the release film. The results are shown in Table 1.

[0101]

(Preparation of Polyethylene Terephthalate Pellets (PET (I))

As an esterification reactor, a continuous esterification reactor including a three-stage complete mixing tank including a stirrer, a partial condenser, a raw material charging port, and a product outlet was used. The amount of TPA (terephthalic acid) was set to 2 tons/hour, and the amount of EG (ethylene glycol) was set to 2 mol per 1 mol of TPA. The amount of antimony trioxide was set such that the amount of Sb atoms with respect to produced PET was set to 160 ppm. These slurries were continuously supplied to a first reaction can of the esterification reactor, and reacted at normal pressure at 255°C for an average residence time of 4 hours. Next, the reaction product in the first esterification reaction can was continuously taken out of the system, and supplied to a second esterification reaction can. 8% by mass of EG distilled off from the first esterification reaction can with respect to produced PET was supplied into the second esterification reaction can. Furthermore, an EG solution containing magnesium acetate tetrahydrate set such that the amount of Mg atoms with respect to the produced PET was set

to 65 ppm and an EG solution containing TMPA (trimethyl phosphate) set such that the amount of P atoms with respect to the produced PET was set to 40 ppm were added, and reacted at 260°C at normal pressure for an average residence time of 1 hour. Then, the reaction product of the second esterification reaction can was continuously taken out of the system, and supplied to a third esterification reaction can. 0.2% by mass of porous colloidal silica having an average particle size of 0.9 μm and subjected to a dispersion treatment with the average number of treatments of 5 passes under pressure of 39 MPa (400 kg/cm²) using a high pressure disperser (manufactured by Nippon Seiki Co., Ltd.), and 0.4% by mass of synthetic calcium carbonate having an average particle size of 0.6 μm and obtained by attaching 1% by mass of a polyacrylic acid ammonium salt per calcium carbonate were added as 10% EG slurries, and reacted at 260°C at normal pressure for an average residence time of 0.5 hours. The esterification reaction product produced in the third esterification reaction can was continuously supplied to a three-stage continuous polycondensation reaction apparatus to perform polycondensation. The polycondensation product was filtered with a filter having a 95% cut diameter of 20 μm obtained by sintering stainless steel fibers, and then subjected to ultrafiltration. Then, the filtered product

was extruded into water, cooled, and then cut into a chip shape to obtain a PET chip having an intrinsic viscosity of 0.60 dl/g (hereinafter abbreviated as PET (I)). The content of the lubricant in the PET chip was 0.6% by mass.

[0102]

(Preparation of Polyethylene Terephthalate Pellets (PET (II)))

Meanwhile, in the production of the PET chip, a PET chip having an intrinsic viscosity of 0.62 dl/g and containing no particles made of calcium carbonate and silica and the like was obtained (hereinafter abbreviated as PET (II)).

[0103]

(Production of Laminated Film Z)

These PET chips were dried, then melted at 285°C, melted at 290°C by a separate melt extruder, and subjected to two-stage filtration of a filter having a 95% cut diameter of 15 μm obtained by sintering stainless steel fibers and a filter having a 95% cut diameter of 15 μm obtained by sintering stainless steel particles, and merged in a feed block. The PET (I) and the and PET (II) were laminated such that the PET (I) was a layer opposite to release surface side and the PET (II) was a layer at release surface side, extruded (cast) into a sheet shape at a speed of 45 m/min, and electrostatically adhered and

cooled on a casting drum at 30°C by an electrostatic adhesion method, to obtain an un-stretched polyethylene terephthalate sheet having an intrinsic viscosity of 0.59 dl/g. The layer ratio was adjusted such that PET (I)/(II) = 60%/40% was set in the calculation of the discharge amount of each extruder. Then, this un-stretched sheet was heated with an infrared heater, and then stretched by 3.5 times in a machine direction at a roll temperature of 80°C according to the speed difference between rolls. Thereafter, the sheet was guided to a tenter, and stretched by 4.2 times in a transverse direction at 140°C. Then, a heat treatment was performed at 210°C in a heat fixation zone. Thereafter, a 2.3% relaxation treatment was performed at 170°C in a transverse direction to obtain a biaxially-stretched polyethylene terephthalate film Z having a thickness of 31 µm. Sa of the release surface side layer of the obtained film Z was 2 nm, and Sa of the opposite release surface side layer was 28 nm.

[0104]

(Polymerization of Polymer Resin A0-1)

194.2 parts by mass of dimethyl terephthalate, 184.5 parts by mass of dimethyl isophthalate, 14.8 parts by mass of dimethyl-5-sodium sulfoisophthalate, 185.1 parts by mass of ethylene glycol, 185.1 parts by mass of neopentyl glycol, and 0.2 parts by mass of tetra-n-butyl titanate

were charged into a stainless steel autoclave equipped with a stirrer, a thermometer, and a partial reflux condenser, and subjected to an ester exchange reaction as the temperature was raised from 160°C to 220°C over 4 hours. Then, the temperature was raised to 255°C, and the pressure of the reaction system was gradually reduced. The mixture was then reacted for 1 hour and 30 minutes under reduced pressure of 30 Pa to obtain a copolymerized polyester resin (A0-1). The obtained copolymerized polyester resin (A0-1) was light yellow and transparent. The reduced viscosity of the copolymerized polyester resin (A0-1) was measured, and found to be 0.60 dl/g. The glass transition temperature by DSC was 65°C.

[0105]

(Production of Polyester Water Dispersion A-1)

30 parts by mass of a polyester resin (A0-1) and 15 parts by mass of ethylene glycol-n-butyl ether were put into a reactor equipped with a stirrer, a thermometer, and a reflux device, and heated and stirred at 110°C to dissolve the resin. The resin was completely dissolved, and 55 parts by mass of water was then gradually added to the polyester solution during stirring. After the addition, the solution was cooled to room temperature during stirring to prepare a milky white polyester water dispersion (A-1) having a solid content of 30% by mass.

[0106]

(Polymerization of Polymer Resin A0-2)

163 parts by mass of dimethyl terephthalate, 163 parts by mass of dimethyl isophthalate, 169 parts by mass of 1,4 butanediol, 324 parts by mass of ethylene glycol, and 0.5 parts by mass of tetra-n-butyl titanate were charged into a stainless steel autoclave equipped with a stirrer, a thermometer, and a partial reflux condenser, and subjected to an ester exchange reaction as the temperature was raised from 160°C to 220°C over 4 hours.

Then, 14 parts by mass of fumaric acid and 203 parts by mass of sebacic acid were added thereto, and the mixture was subjected to an esterification reaction as the temperature was raised from 200°C to 220°C over 1 hour. Then, the temperature was raised to 255°C, and the pressure of the reaction system was gradually reduced. The mixture was then reacted for 1 hour and 30 minutes under reduced pressure of 29 Pa to obtain a hydrophobic copolymerized polyester resin (A0-2). The obtained hydrophobic copolymerized polyester resin (A0-2) was light yellow and transparent.

[0107]

(Production of Polyester Water Dispersion A-2)

Then, 60 parts by mass of the copolymerized polymer polyester resin (A0-2), 45 parts by mass of methyl ethyl

ketone, and 15 parts by mass of isopropyl alcohol were put into a reactor equipped with a production stirrer for a graft resin, a thermometer, a reflux device, and a quantitative dropping device. The mixture was heated and stirred at 65°C to dissolve the resin. The resin was completely dissolved, and 24 parts by mass of maleic anhydride was added to the polyester solution.

Then, a solution prepared by dissolving 16 parts by mass of styrene and 1.5 parts by mass of azobisdimethylvaleronitrile in 19 parts by mass of methyl ethyl ketone was dropped into the polyester solution at 0.1 ml/min, and stirring continued to be carried out for another 2 hours. Sampling for analysis from the reaction solution was carried out, and 8 parts by mass of methanol was then added. Then, 300 parts by mass of water and 24 parts by mass of triethylamine were added to the reaction solution, and stirred for 1 hour.

Thereafter, the internal temperature of the reactor was raised to 100°C, and methyl ethyl ketone, isopropyl alcohol and excess triethylamine were distilled off by distillation to obtain a pale yellow transparent polyester-based resin. A uniform water-dispersible polyester-based graft copolymer dispersion solution (A-2) having a solid content concentration of 25% by mass was prepared. The glass transition temperature of the obtained polyester-

based graft copolymer was 68°C.

[0108]

(Production of Polyurethane Water Dispersion A-3)

43.75 parts by mass of 4,4-dicyclohexylmethane diisocyanate, 12.85 parts by mass of dimethylolbutanoic acid, 153.41 parts by mass of polyhexamethylene carbonate diol having a number-average molecular weight of 2000, 0.03 parts by mass of dibutyltin dilaurate, and 84.00 parts by mass of acetone as a solvent were charged into a four-neck flask equipped with a stirrer, a Dimroth condenser, a nitrogen introducing pipe, a silica gel drying pipe, and a thermometer, and stirred under a nitrogen atmosphere at 75°C for 3 hours. It was confirmed that the reaction solution reached a predetermined amine equivalent. Next, the temperature of the reaction solution was decreased to 40°C, and 8.77 parts of triethylamine was then added to the reaction solution to obtain a polyurethane prepolymer solution. Next, 450 g of water was added to a reaction vessel equipped with a homodisper allowing high-speed stirring, and adjusted to 25°C. The polyurethane prepolymer solution was added to the reaction vessel and dispersed in water with stirring for mixing at 2000 min⁻¹. Thereafter, acetone and part of water were removed under reduced pressure, thereby preparing a water-soluble polyurethane resin solution A-3 having a solid content of

37% by mass. The glass transition temperature of the obtained polyurethane resin was -30°C .

[0109]

(Production of Acrylic Polyol A-4)

231 parts by mass of methyl methacrylate (MMA), 130 parts by mass of stearyl methacrylate (SMA), 100 parts by mass of hydroxyethyl methacrylate (HEMA), 33 parts by mass of methacrylic acid (MAA), and 1153 parts by mass of isopropyl alcohol (IPA) were charged into a four-neck flask equipped with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, and the temperature in the flask was raised to 80°C during stirring. The stirring was carried out for 3 hours while the temperature in the flask was maintained at 80°C , and 0.5 parts by mass of 2,2'-azobis-2-methyl-N-(2-hydroxyethyl)propionamide was then added into the flask. The atmosphere in the flask was substituted by nitrogen while the temperature in the flask was raised to 120°C , and the mixture was then stirred at 120°C for 2 hours.

Then, a decompression operation of 1.5 kPa was performed at 120°C to remove unreacted raw materials and solvent, thereby obtaining an acrylic polyol. The inside of the flask was returned to atmospheric pressure, and cooled to room temperature. 1976 parts by mass of an IPA aqueous solution (water content: 50% by mass) was added,

followed by mixing. Thereafter, triethylamine was added using a dropping funnel during stirring, and the acrylic polyol was neutralized until the pH of the solution was in a range of 5.5 to 7.5, to obtain an acrylic polyol (A-4) having a solid content concentration of 20% by mass.

[0110]

(Production of Oxazoline-Based Cross-Linking Agent B-1)

460.6 parts of isopropyl alcohol was charged into a flask equipped with a stirrer, a reflux condenser, a nitrogen introducing pipe, and a thermometer, and heated to 80°C while causing nitrogen gas to gently flow thereinto. A monomer mixture prepared beforehand containing 126 parts of methyl methacrylate, 210 parts of 2-isopropenyl-2-oxazoline, and 84 parts of methoxy polyethylene glycol acrylate, and an initiator solution prepared beforehand containing 21 parts of 2,2'-azobis(2-methylbutyronitrile) ("ABN-E", manufactured by Japan Finechem Inc.) that is a polymerization initiator, and 189 parts of isopropyl alcohol, were dropped from dropping funnels, respectively, over 2 hours to cause reaction. After the end of dropping, the reaction continued to be carried out for 5 hours. The flow of nitrogen gas was continued during the reaction, and the temperature in the flask was kept at $80 \pm 1^\circ\text{C}$. Thereafter, the reaction solution was cooled to obtain a resin (B-1) having an oxazoline group having a solid

content concentration of 25%. The oxazoline group amount of the obtained resin (B-1) having an oxazoline group was 4.3 mmol/g, and the number-average molecular weight thereof measured by GPC (gel permeation chromatography) was 20000.

[0111]

(Silica particles C-1)

Colloidal silica (trade name: Snowtex XL, manufactured by Nissan Chemical Corporation, average particle size: 40 nm, solid content concentration: 40% by mass)

[0112]

(Silica particles C-2)

Colloidal silica (trade name: Snowtex ZL, manufactured by Nissan Chemical Corporation, average particle size: 100 nm, solid content concentration: 40% by mass)

[0113]

(Silica particles C-3)

Colloidal silica (trade name: MP2040, manufactured by Nissan Chemical Corporation, average particle size: 200 nm, solid content concentration: 40% by mass)

[0114]

(Silica particles C-4)

Colloidal silica (trade name: MP4540M, manufactured by Nissan Chemical Corporation, average particle size: 450

nm, solid content concentration: 40% by mass)

[0115]

(Acrylic particles C-5)

Acrylic particle water dispersion (trade name: MX100W, manufactured by Nippon Shokubai Co., Ltd., average particle size: 150 nm, solid content concentration: 10% by mass)

[0116]

(Binder component of release coating layer)

The following materials were used as the binder component of the release coating layer.

(X-1) Melamine-based compound

Hexamethoxymethylmelamine (manufactured by Tokyo Chemical Industry Co., Ltd., solid content: 100% by mass)

(X-2) Epoxy-based compound (alicyclic epoxy compound)

3',4'-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate

(Product name: CELLOXIDE (registered trademark) 2021P, manufactured by Daicel Corporation, solid content: 100% by mass)

(X-3) Acrylate-based compound (polyfunctional)

Dipentaerythritol hexaacrylate (Product name: DPFA, manufactured by DAICEL-ALLNEX LTD., solid content: 100% by mass)

(X-4) Thermosetting addition reaction type silicone

(Product name: KS-847H, manufactured by Shin-Etsu Silicone Co., Ltd., solid content: 30% by mass)

[0117]

(Rear surface smoothing coating solution Y)

94 parts by mass of dipentaerythritol hexaacrylate [solid content: 100% by mass] as an active energy ray curable compound, 1 part by mass of polydimethyl siloxane having a polyether-modified acryloyl group [manufactured by BYK-Chemie GmbH, trade name: "BYK-UV3500", solid content: 100% by mass] as a polyorganosiloxane, and 5 parts by mass of an α -aminoalkylphenone-based photopolymerization initiator [2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1-one manufactured by BASF Corporation, trade name: "IRGACURE907", solid content: 100% by mass] as a photopolymerization initiator, were diluted with a mixed solvent of isopropyl alcohol and methyl ethyl ketone (mass ratio: 3/1), to obtain a rear surface-smoothing-coat-layer-forming material having a solid content of 20% by mass.

[0118]

(Example 1)

(Preparation of Easy-to-slip Coating solution 1)

An easy-to-slip coating solution 1 having the following composition was prepared.

(Easy-to-slip coating solution 1)

Water 48.33 parts by mass

Isopropyl alcohol 35.00 parts by mass

Polyester water dispersion A-1 15.78 parts by
mass

(Solid content concentration: 30% by mass)

Silica particles C-3 0.59 parts by mass

(Average particle size: 200 nm, solid content
concentration: 40% by mass)

Surfactant D-1 (fluorine-based, solid content
concentration: 10% by mass) 0.30 parts by mass

[0119]

(Production of Polyester Film)

As a film raw material polymer, a PET resin pellet
(PET (II)) having an intrinsic viscosity (solvent:
phenol/tetrachloroethane = 60/40) of 0.62 dl/g and
substantially containing no inorganic particles was dried
at 135°C for 6 hours under reduced pressure of 133 Pa.
Thereafter, the PET resin pellet was supplied to an
extruder, and melt-extruded into a sheet shape at about
280°C. The melt-extruded product was rapidly quenched,
adhered, and solidified on a rotating cooling metal roll
maintained at a surface temperature of 20°C to obtain an
un-stretched PET sheet.

[0120]

This un-stretched PET sheet was heated to 100°C with
a heated roll group and an infrared heater, and then

stretched by 3.5 times in a longitudinal direction with a roll group having a circumferential velocity difference to obtain a uniaxially stretched PET film.

[0121]

Then, the easy-to-slip coating solution was coated on one surface of a PET film with a bar coater, and then dried at 80°C for 15 seconds. The coating amount after final stretching and drying was adjusted to 0.1 μm .

Subsequently, with a tenter, the film was stretched by 4.0 times in a transverse direction at 150°C. The film was heated at 230°C for 0.5 seconds in a state where the length in the transverse direction was fixed. The film was further subjected to a loosening treatment in the transverse direction by 3% at 230°C for 10 seconds to obtain an in-line coating polyester film having a thickness of 31 μm .

[0122]

(Formation of Release Coating Layer)

A release coating solution 1 was coated on a surface opposite to a surface on which the easy-to-slip coating layer was laminated, of the in-line coating polyester film obtained above with a reverse gravure coater such that a thickness after drying was 0.6 μm . Then, the release coating solution was dried at 140°C for 15 seconds to form a release coating layer, thereby obtaining a release film

for producing a super-thin layer ceramic green sheet. The release film for producing a super-thin layer ceramic green sheet had excellent winding properties and the like, processability, and handling properties with no particular problems. When a ceramic slurry was coated on the obtained release film to evaluate pinholes and thickness variation, good evaluation results were obtained.

(Release coating solution 1)

Methyl ethyl ketone 44.50 parts by mass

Toluene 44.50 parts by mass

Binder (X-1) 10.00 parts by mass

(Hexamethoxymethylmelamine, solid content: 100%,
manufactured by Tokyo Chemical Industry Co., Ltd., trade
name: N,N,N',N',N'',N''-hexakis(methoxymethyl)melamine)

Release agent 0.50 parts by mass

(One terminal carboxyl-modified polydimethylsiloxane, X22-
3710, solid content: 100%, manufactured by Shin-Etsu
Chemical Co., Ltd.)

Acid catalyst (p-toluenesulfonic acid) 0.50 parts
by mass

[0123]

(Example 2)

A release film for producing a super-thin layer
ceramic green sheet was obtained in the same manner as in
Example 1 except that the easy-to-slip coating solution 1

was changed to the following easy-to-slip coating solution 2.

(Easy-to-slip coating solution 2)

Water 45.18 parts by mass

Isopropyl alcohol 35.00 parts by mass

Polyester water dispersion A-2 (solid content concentration: 25% by mass) 18.93 parts by mass

Silica particles C-3 0.59 parts by mass
(Average particle size: 200 nm, solid content concentration: 40% by mass)

Surfactant D-1 (fluorine-based, solid content concentration: 10% by mass) 0.30 parts by mass

[0124]

(Example 3)

A release film for producing a super-thin layer ceramic green sheet was obtained in the same manner as in Example 1 except that the easy-to-slip coating solution 1 was changed to the following easy-to-slip coating solution 3.

(Easy-to-slip coating solution 3)

Water 51.32 parts by mass

Isopropyl alcohol 35.00 parts by mass

Polyurethane resin water dispersion A-3 12.79 parts by mass

(Solid content concentration: 37% by mass)

Silica particles C-3 0.59 parts by mass
(Average particle size: 200 nm, solid content
concentration: 40% by mass)

Surfactant D-1 (fluorine-based, solid content
concentration: 10% by mass) 0.30 parts by mass

[0125]

(Example 4)

A release film for producing a super-thin layer
ceramic green sheet was obtained in the same manner as in
Example 1 except that the easy-to-slip coating solution 1
was changed to the following easy-to-slip coating solution
4.

(Easy-to-slip coating solution 4)

Water 41.86 parts by mass

Isopropyl alcohol 35.00 parts by mass

Acrylic polyol resin A-4 16.57 parts by mass

(Solid content concentration: 20% by mass)

Oxazoline-based cross-linking agent B-1 5.68 parts
by mass

(Solid content concentration: 25% by mass)

Silica particles C-3 0.59 parts by mass
(Average particle size: 200 nm, solid content
concentration: 40% by mass)

Surfactant D-1 (fluorine-based, solid content
concentration: 10% by mass) 0.30 parts by mass

[0126]

(Example 5)

A release film for producing a super-thin layer ceramic green sheet was obtained in the same manner as in Example 1 except that the easy-to-slip coating solution 1 was changed to the following easy-to-slip coating solution 5.

(Easy-to-slip coating solution 5)

Water 41.74 parts by mass

Isopropyl alcohol 35.00 parts by mass

Acrylic polyol resin A-4 16.57 parts by mass

(Solid content concentration: 20% by mass)

Oxazoline-based cross-linking agent B-1 (solid content concentration: 25% by mass) 5.68 parts by mass

Silica particles C-3 0.59 parts by mass

(Average particle size: 200 nm, solid content concentration: 40% by mass)

Silica particles C-4 0.12 parts by mass

(Average particle size: 450 nm, solid content concentration: 40% by mass)

Surfactant D-1 (fluorine-based, solid content concentration: 10% by mass) 0.30 parts by mass

[0127]

(Example 6)

A release film for producing a super-thin layer

ceramic green sheet was obtained in the same manner as in Example 1 except that the easy-to-slip coating solution 1 was changed to the following easy-to-slip coating solution 6.

(Easy-to-slip coating solution 6)

Water 41.15 parts by mass

Isopropyl alcohol 35.00 parts by mass

Acrylic polyol resin A-4 16.57 parts by mass

(Solid content concentration: 20% by mass)

Oxazoline-based cross-linking agent B-1 (solid content concentration: 25% by mass) 5.68 parts by mass

Silica particles C-1 1.18 parts by mass

(Average particle size: 40 nm, solid content concentration: 40% by mass)

Silica particles C-4 0.12 parts by mass

(Average particle size: 450 nm, solid content concentration: 40% by mass)

Surfactant D-1 (fluorine-based, solid content concentration: 10% by mass) 0.30 parts by mass

[0128]

(Example 7)

A release film for producing a super-thin layer ceramic green sheet was obtained in the same manner as in Example 1 except that the easy-to-slip coating solution 1 was changed to the following easy-to-slip coating solution

7.

(Easy-to-slip coating solution 7)

Water 41.27 parts by mass

Isopropyl alcohol 35.00 parts by mass

Acrylic polyol resin A-4 16.57 parts by mass

(Solid content concentration: 20% by mass)

Oxazoline-based cross-linking agent B-1 (solid
content concentration: 25% by mass) 5.68 parts by mass

Silica particles C-2 1.18 parts by mass

(Average particle size: 100 nm, solid content
concentration: 40% by mass)

Surfactant D-1 (fluorine-based, solid content
concentration: 10% by mass) 0.30 parts by mass

[0129]

(Example 8)

A release film for producing a super-thin layer
ceramic green sheet was obtained in the same manner as in
Example 1 except that the easy-to-slip coating solution 1
was changed to the following easy-to-slip coating solution
8.

(Easy-to-slip coating solution 8)

Water 40.09 parts by mass

Isopropyl alcohol 35.00 parts by mass

Acrylic polyol resin A-4 16.57 parts by mass

(Solid content concentration: 20% by mass)

Oxazoline-based cross-linking agent B-1 (solid
content concentration: 25% by mass) 5.68 parts by mass

Acrylic particles C-5 2.37 parts by mass
(Average particle size: 150 nm, solid content
concentration: 10% by mass)

Surfactant D-1 (fluorine-based, solid content
concentration: 10% by mass) 0.30 parts by mass

[0130]

(Example 9)

A release film for producing a super-thin layer
ceramic green sheet was obtained in the same manner as in
Example 4 except that a release coating solution 2 was
coated on a surface opposite to the easy-to-slip coating
layer, of the obtained in-line coating polyester film with
a reverse gravure coater such that a thickness after drying
was 0.6 μm , and then dried at 90°C for 15 seconds, and
irradiated with ultraviolet rays of 60 mJ/cm², to form a
release coating layer.

(Release coating solution 2)

Methyl ethyl ketone 44.50 parts by mass

Toluene 44.50 parts by mass

Binder component (X-2) 10.00 parts by mass

(Product name: CELLOXIDE (registered trademark) 2021P,
manufactured by Daicel Corporation, solid content: 100% by
mass))

Release agent 0.50 parts by mass
(Alicyclic epoxy group-containing silicone resin, POLY215,
solid content: 100%, manufactured by Arakawa Chemical
Industries)

Photo-cationic initiator (CAT211) 0.50 parts by
mass

[0131]

(Example 10)

A release film for producing a super-thin layer
ceramic green sheet was obtained in the same manner as in
Example 4 except that a release coating solution 3 was
coated on a surface opposite to the easy-to-slip coating
layer, of the obtained in-line coating polyester film such
that a thickness after drying was 1.0 μm , and irradiated
with ultraviolet rays having an irradiation amount of 60
 mJ/cm^2 under a nitrogen gas atmosphere (oxygen
concentration: 1%).

(Release coating solution 3)

Methyl ethyl ketone 39.40 parts by mass

Toluene 39.40 parts by mass

Binder component (X-3) 20.00 parts by mass

(Product name: DPHA, manufactured by DAICEL-ALLNEX LTD.,
solid content: 100% by mass)

Release agent (acryl-modified polydimethylsiloxane)
0.20 parts by mass

(BYK (registered trademark)-UV3500, manufactured by BYK-Chemie GmbH, solid content: 100% by mass)

Photo-radical initiator 1.00 part by mass
(Irgacure (registered trademark) 907, manufactured by BASF Corporation)

[0132]

(Comparative Example 1)

A release film for production of a ceramic green sheet was obtained in the same manner as in Example 1 except that E5000-25 μm (manufactured by Toyobo Co., Ltd.) was used as a film for forming a release coating layer in place of the in-line coating film that was prepared in Example 1 and had one surface having an easy-to-slip coating layer formed thereon. The E5000 contained particles in the film, and Sa of each of both surfaces was 0.031 μm .

[0133]

(Comparative Example 2)

A release film for producing a super-thin layer ceramic green sheet was obtained in the same manner as in Example 10 except that E5000-25 μm (manufactured by Toyobo Co., Ltd.) was used as the film for forming the release coating layer in place of the in-line coating film having the easy-to-slip coating layer on one surface, prepared in Example 1.

[0134]

(Comparative Example 3)

A release film for production of a ceramic green sheet was obtained in the same manner as in Example 1 except that a laminated film Z was used as a film for forming a release coating layer in place of the in-line coating film that was prepared in Example 1 and had one surface having an easy-to-slip coating layer formed thereon. A release coating layer was provided on a surface of the laminated film Z on which a PET (II) pellet was discharged (a layer containing no particles).

[0135]

(Comparative Example 4)

A rear surface smoothing coating solution Y was coated on the surface opposite to the surface on which the release coating layer of the release film for producing a super-thin layer ceramic green sheet obtained in Comparative Example 3 was formed, with a reverse gravure coater such that a thickness after drying was 0.5 μm , then dried with hot air at 90°C for 30 seconds, and immediately subjected to ultraviolet irradiation (300 mJ/cm²) with an electrodeless lamp (H bulb, manufactured by Heraeus Co., Ltd.) to form a rear surface smoothing layer, thereby obtaining a release film for producing a super-thin layer ceramic green sheet.

[0136]

(Comparative Example 5)

A release film for producing a super-thin layer ceramic green sheet was obtained in the same manner as in Comparative Example 4 except that the rear surface smoothing layer having a thickness of 0.7 μm was coated.

[0137]

(Comparative Example 6)

A release film for producing a super-thin layer ceramic green sheet was obtained in the same manner as in Comparative Example 4 except that the rear surface smoothing layer having a thickness of 1.0 μm was coated.

[0138]

(Comparative Example 7)

A release film for producing a super-thin layer ceramic green sheet was obtained in the same manner as in Example 4 except that a release coating solution 4 was coated on a surface opposite to the easy-to-slip coating layer, of the obtained in-line coating polyester film with a reverse gravure coater such that a thickness after drying was 0.6 μm , and then dried at 160°C for 15 seconds, to form a release coating layer.

(Release coating solution 4)

Methyl ethyl ketone	33.00 parts by mass
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Toluene	33.00 parts by mass
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Binder component (X-4) 33.30 parts by mass

Thermosetting addition reaction type silicone

(Product name: KS-847H, manufactured by Shin-Etsu Silicone Co., Ltd., solid content: 30% by mass)

Catalyst 0.70 parts by mass

(Platinum catalyst, CAT-PL-50T, manufactured by Shin-Etsu Chemical Co., Ltd.)

[0139]

Table 1 shows the evaluation results of Examples and Comparative Examples.

[0140]

[Table 1]

	PET FILM	EASY-TO-SLIP COATING LAYER*				RELEASE COATING LAYER					
		Sa (μm)	P (μm)	RSm (μm)	EASY-TO-SLIP COATING LAYER THICKNESS (μm)	Sa (μm)	ELASTIC MODULUS			RELEASE COATING LAYER THICKNESS (μm)	
							P (μm)	(GPa)	<EVALUATIONS>		
EXAMPLE 1	SINGLE LAYER, NO LUBRICANT	0.005	0.092	2.2	0.1	0.001	0.016	2.5	GOOD	0.6	GOOD
EXAMPLE 2	SINGLE LAYER, NO LUBRICANT	0.003	0.105	2.2	0.1	0.001	0.016	2.5	GOOD	0.6	GOOD
EXAMPLE 3	SINGLE LAYER, NO LUBRICANT	0.004	0.110	2.2	0.1	0.001	0.016	2.5	GOOD	0.6	GOOD
EXAMPLE 4	SINGLE LAYER, NO LUBRICANT	0.004	0.123	2.2	0.1	0.001	0.016	2.5	GOOD	0.6	GOOD
EXAMPLE 5	SINGLE LAYER, NO LUBRICANT	0.004	0.196	2.3	0.1	0.001	0.016	2.5	GOOD	0.6	GOOD
EXAMPLE 6	SINGLE LAYER, NO LUBRICANT	0.004	0.198	2.3	0.1	0.001	0.016	2.5	GOOD	0.6	GOOD
EXAMPLE 7	SINGLE LAYER, NO LUBRICANT	0.004	0.080	2.1	0.1	0.001	0.016	2.5	GOOD	0.6	GOOD
EXAMPLE 8	SINGLE LAYER, NO LUBRICANT	0.004	0.102	2.1	0.1	0.001	0.016	2.5	GOOD	0.6	GOOD
EXAMPLE 9	SINGLE LAYER, NO LUBRICANT	0.004	0.123	2.2	0.1	0.001	0.019	3.7	GOOD	0.6	GOOD
EXAMPLE 10	SINGLE LAYER, NO LUBRICANT	0.004	0.123	2.2	0.1	0.001	0.026	5.4	GOOD	1.0	GOOD
COMPARATIVE EXAMPLE 1 ^{*1}	E5000	(0.031)	(0.769)	(30.2)	—	0.017	0.233	2.5	GOOD	0.6	EXTREMELY POOR
COMPARATIVE EXAMPLE 2 ^{*1}	E5000	(0.031)	(0.769)	(30.2)	—	0.006	0.058	5.4	GOOD	1.0	VERY POOR
COMPARATIVE EXAMPLE 3 ^{*1}	LAMINATED FILM Z	(0.028)	(0.754)	(30.0)	—	0.001	0.016	2.5	GOOD	0.6	VERY POOR
COMPARATIVE EXAMPLE 4 ^{*2}	LAMINATED FILM Z	(0.014)	(0.280)	(30.3)	(0.5)	0.001	0.016	2.5	GOOD	0.6	VERY POOR
COMPARATIVE EXAMPLE 5 ^{*2}	LAMINATED FILM Z	(0.010)	(0.150)	(20.0)	(0.7)	0.001	0.016	2.5	GOOD	0.6	POOR
COMPARATIVE EXAMPLE 6 ^{*2}	LAMINATED FILM Z	(0.006)	(0.058)	(12.5)	(1.0)	0.001	0.016	2.5	GOOD	0.6	POOR
COMPARATIVE EXAMPLE 7	SINGLE LAYER, NO LUBRICANT	0.004	0.123	2.2	0.1	0.002	0.027	0.4	POOR	0.6	GOOD

*1: In the “easy-to-slip coating layer” columns of Comparative Examples 1 to 3, the evaluation results of the surface opposite to the laminated surface of the “release coating layer” of the polyester film are described.

*2: In the “easy-to-slip coating layer” columns of Comparative Examples 4 to 6, the evaluation results of the surface of the “rear surface smoothing layer” are described.

[0141]

In Examples 1 to 10, all the parameters of Sa, P, and RSm of the surface of the easy-to-slip coating layer were in appropriate ranges, whereby the ceramic green sheet causing no pinholes could be obtained. In Comparative Examples 1 to 3, all the parameters of Sa, P, and RSm of the easy-to-slip surface were large, so that the occurrence of pinholes was observed. In Comparative Examples 4 to 6, Sa and P could be kept in appropriate ranges by filling the unevenness of the easy-to-slip surface with the smoothing layer. However, RSm was large, so that the occurrence of pinholes was insufficiently suppressed. Large RSm means that a distance between projections is large and the number of the projections per unit area is small. It is considered that a pressure applied to each projection is increased, which causes the pinholes. In Comparative Example 7, all the parameters of Sa, P, and RSm of the surface of the easy-to-slip coating layer were in appropriate ranges, whereby the ceramic green sheet causing no pinholes could be obtained. However, the film elastic modulus of the surface of the release coating film was low, so that normal peeling could not be provided to cause a decreased yield.

INDUSTRIAL APPLICABILITY

[0142]

The present invention can provide a release film for producing a ceramic green sheet, which can achieve both good winding properties and prevention of pinholes and partial thickness variation and the like even when the ceramic green sheet is reduced in thickness. The use of the release film for production of a ceramic green sheet of the present invention can provide a super-thin layer ceramic green sheet and efficiently produce a minute ceramic capacitor.

CLAIMS

1. A release film for producing a ceramic green sheet, the release film comprising:

a polyester film substantially containing no inorganic particles as a substrate;

a release coating layer on one surface of the substrate; and

an easy-to-slip coating layer containing particles on another surface of the substrate,

wherein:

a film elastic modulus measured from a surface opposite to the substrate in the release coating layer by a nanoindentation test on the release coating layer is 2.0 GPa or more; and

the easy-to-slip coating layer has average area surface roughness (Sa) of 1 nm or more and 25 nm or less, a maximum protrusion height (P) of 60 nm or more and 500 nm or less, and an average length of a roughness curve element (RSm) of 10 μm or less.

2. The release film for producing a ceramic green sheet according to claim 1, wherein the release coating layer has average area surface roughness (Sa) of 5 nm or less and a maximum protrusion height (P) of 30 nm or less.

3. The release film for producing a ceramic green sheet according to claim 1 or 2, wherein the easy-to-slip coating layer has a thickness of 0.001 μm or more and 2 μm or less.

4. A method for producing a ceramic green sheet using the release film for producing a ceramic green sheet according to any one of claims 1 to 3.

5. The method for producing a ceramic green sheet according to claim 4, wherein the ceramic green sheet to be produced has a thickness of 0.2 μm to 2.0 μm .

6. A method for producing a ceramic capacitor, wherein the method for producing a ceramic green sheet according to claim 4 or 5 is employed.