

DESCRIPTION

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

TECHNICAL FIELD

[0001]

The present invention relates to a release film for producing a ceramic green sheet. More specifically, the present invention relates to a release film for producing a ceramic green sheet, which can achieve both prevention of pinholes and partial thickness variation and the like and reduction of unwinding electric charge 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 coarse to eliminate a problem of sticking (blocking) and the like of front and rear surfaces of a release film for producing 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 rear surface protrusions cause

pinholes and partial thickness variation.

[0003]

In order to reduce the heights of the rear surface 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 DOCUMENT

[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, it is an

object of the present invention to produce an excellent release film for producing a ceramic green sheet, which can achieve both prevention of pinholes and partial thickness variation and the like and reduction of unwinding electric charge 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 other surface of the substrate,

wherein:

the easy-to-slip coating layer has an average area surface roughness (S_a) 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 (RSm) of a roughness curve element of 10 μm or less; and

a single film of a mixture composition comprising a resin and a cross-linking agent both used in the easy-to-slip coating layer has a Martens hardness (HM) of 150 N/mm² or more and a ratio of elastic to total work (η_{it}) of 28% or more.

2. The release film for producing a ceramic green sheet according to the above 1, wherein the easy-to-slip coating layer is obtained by curing a composition containing an acrylic resin and at least one cross-linking agent selected from an oxazoline-based cross-linking agent or a carbodiimide-based cross-linking agent.

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 or more and 2.0 μm or less.

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 an excellent release film for producing a ceramic green sheet, which can achieve both prevention of pinholes and partial thickness variation and the like and reduction of unwinding electric charge 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 producing 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 an easy-to-slip coating layer containing particles on the other surface.

[0009]

In order to increase the protrusion density of an

easy-to-slip surface, the present inventors have proposed that a release film capable of coping with the recent reduction in the thickness of a green sheet is provided by setting an average length (RSm) of a roughness curve element of the easy-to-slip coating surface in a specific range (International Application No. PCT/JP2017/017354). By increasing the protrusion density by such a technique, good winding properties and prevention of pinholes and partial thickness variation and the like can be provided at first glance while the protrusion height is maintained low, which is preferable.

[0010]

In the present invention, a single film of a mixture composition comprising a resin and a cross-linking agent both used in the easy-to-slip coating layer has a Martens hardness (HM) of 150 N/mm² or more and a ratio of elastic to total work (η_{it}) of 28% or more, whereby the hardness of the easy-to-slip coating layer becomes moderately high, and the deformation of the easy-to-slip coating layer occurring when the easy-to-slip coating layer is brought into contact with the release coating layer is instantaneously recovered when the pressure is reduced.

[0011]

The high Martens hardness contributes to the fact that the deformation of the easy-to-slip coating layer is

less likely to occur when the film is wound after the release coating layer is coated.

[0012]

The high ratio of elastic to total work η it means that, in added work, the rate of elastic deformation is greater than that of plastic deformation, and the deformation of the easy-to-slip coating layer deformed by contact with the release coating layer is immediately recovered when the pressure with the release coating layer becomes weaker. The present inventors have found that not only the Martens hardness which indicates hardness but also the ratio of elastic to total work which is an index indicating whether the deformation is immediately recovered affect unwinding electric charge when the film roll is unwound.

[0013]

When the diameter of the film roll is reduced during unwinding of the film roll, the deformation of the easy-to-slip coating layer is recovered in the state of the roll before unwinding, and the contact area between the easy-to-slip coating layer and the release layer during unwinding is small. This is considered to contribute to the reduction of the unwinding electric charge.

[0014]

In general, it is known that, as the contact area

between two objects brought into contact with each other increases, electric charge during peeling when the two objects are peeled off increases. If the amount of deformation of the easy-to-slip coating layer is small, and the recovery of the deformation is fast, the contact area between the easy-to-slip coating layer and the release layer when the release film roll is unwound is small, whereby the unwinding electric charge when the release film roll is unwound can be suppressed, which is preferable.

[0015]

The small unwinding electric charge can prevent the abnormal quality of a ceramic capacitor due to the adhesion of environmental foreign matters to a release surface, which is preferable. In the reduction in the thickness of a ceramic sheet as a recent trend, even the adhesion of minute environmental foreign matters to a release surface conventionally causing no problems causes problems, whereby a release film having a composition of the easy-to-slip coating layer specified in the present invention is effective. The average length (R_{Sm}) of the roughness curve element of the easy-to-slip coating layer is more preferably set within a specific range.

[0016]

(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. Among these polyester films, the polyethylene terephthalate film is most preferable from the balance between physical properties and cost.

[0017]

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.

[0018]

(Easy-To-Slip Coating Layer)

The release film of the present invention includes an 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.

[0019]

In the present invention, it is preferable that the single film of a mixture composition comprising a resin and a cross-linking agent both used in the easy-to-slip coating layer have a Martens hardness (HM) of 150 N/mm² or more. More preferably, the Martens hardness (HM) is 200 N/mm² or more. If the single film of a mixture composition comprising a resin and a cross-linking agent both used in the easy-to-slip coating layer has a Martens hardness (HM) of 150 N/mm² or more, the hardness of the easy-to-slip coating layer becomes moderately high, which is preferable.

[0020]

In the present invention, it is preferable that the single film of a mixture composition comprising a resin and a cross-linking agent both used in the easy-to-slip coating layer have a Martens hardness (HM) of 600 N/mm² or less. More preferably, the Martens hardness (HM) is 500 N/mm² or less. If the single film of a mixture composition comprising a resin and a cross-linking agent both used in the easy-to-slip coating layer has a Martens hardness (HM) of 600 N/mm² or less, damages such as scratches or dents are not applied to the surface of the release coating layer, which is preferable.

[0021]

In the present invention, it is preferable that the single film of a mixture composition comprising a resin and a cross-linking agent both used in the easy-to-slip coating layer have a ratio of elastic to total work (η_{it}) of 28% or more. More preferably, the ratio of elastic to total work (η_{it}) is 30% or more. If the single film of a mixture composition comprising a resin and a cross-linking agent both used in the easy-to-slip coating layer has a ratio of elastic to total work (η_{it}) of 28% or more, the deformation of the easy-to-slip coating layer occurring when the easy-to-slip coating layer is brought into contact with the release coating layer is immediately recovered by the reduced pressure during unwinding of the film roll. When the deformation is recovered, the contact area between the easy-to-slip coating layer and the release layer when the film roll is unwound is small, whereby unwinding electric charge when the release film roll is unwound can be suppressed, which is preferable.

[0022]

In the present invention, it is preferable that the single film of a mixture composition comprising a resin and a cross-linking agent both used in the easy-to-slip coating layer have a ratio of elastic to total work (η_{it}) of 90% or less. More preferably, the ratio of elastic to total work (η_{it}) is 80% or less. If the single film of a

mixture composition comprising a resin and a cross-linking agent both used in the easy-to-slip coating layer has a ratio of elastic to total work (η_{it}) of 90% or less, the plastic deformation of the easy-to-slip coating layer is moderate, whereby the friction coefficient of the easy-to-slip coating layer with the release layer is too low. This provides less concerns such as occurrence of winding deviation, which is preferable.

[0023]

(Binder Resin in Easy-To-Slip Coating Layer)

The binder resin constituting the easy-to-slip coating layer in the present invention 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 or an acrylic resin from the viewpoint that the abovementioned Martens hardness and ratio of elastic to total work can be achieved. Among these, it is particularly preferable to use an acrylic resin. The acrylic resin preferably has a hydroxyl group and a carboxyl group in its molecule. Structural units having a hydroxyl group are more preferably contained in an amount of 20 to 90 mol% in 100 mol% of all structural

units. If the amount of the structural units having a hydroxyl group is 20 mol% or more, the water solubility of the acrylic resin can be moderately kept, which is preferable. Meanwhile, when the amount is 90 mol% or less, the hydroxyl group of the acrylic resin and the particles contained in the easy-to-slip coating layer cause no extreme interaction to provide the uniform dispersion of the particles, which is preferable.

[0024]

In order to introduce the hydroxyl group into the acrylic resin, monomers having a hydroxy group such as 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, and 4-hydroxybutyl(meth)acrylate, and a ring-opening adduct of γ -butyrolactone or ϵ -caprolactone to 2-hydroxyethyl(meth)acrylate, and the like may be used as a copolymerization component. Among these, 2-hydroxyethyl(meth)acrylate is preferable since 2-hydroxyethyl(meth)acrylate does not inhibit water solubility. These may be used in combination of two or more thereof.

[0025]

The hydroxyl value of the acrylic resin is preferably 2 mgKOH/g or more, more preferably 5 mgKOH/g or more, and still more preferably 10 mgKOH/g or more. If the hydroxyl value of the acrylic resin is 2 mgKOH/g or more, the water

solubility of the acrylic resin is good, which is preferable.

[0026]

The hydroxyl value of the acrylic resin is preferably 250 mgKOH/g or less, more preferably 230 mgKOH/g or less, and still more preferably 200 mgKOH/g or less. If the hydroxyl value of the acrylic resin is 250 mgKOH/g or less, the hydroxyl group of the acrylic resin and the particles contained in the easy-to-slip coating layer cause no extreme interaction to provide the uniform dispersion of the particles, which is preferable.

[0027]

The acrylic resin used in the present invention preferably has a carboxyl group in addition to the hydroxyl group. The acrylic resin has the carboxyl group, whereby a crosslinked structure with a cross-linking agent can be formed, and water solubility can be easily imparted. Examples thereof include monomers containing carboxy groups such as (meth)acrylic acid, crotonic acid, itaconic acid, maleic acid, and fumaric acid, and monomers containing acid anhydride groups such as maleic anhydride and itaconic anhydride.

[0028]

The amount of the monomer having a carboxyl group is preferably 4 mol% or more, and more preferably 10 mol% or

more in 100 mol% of all the structural units of the acrylic resin. When the amount is 4 mol% or more, it is easy to form a crosslinked structure in the easy-to-slip coating layer and to impart water solubility, which is preferable. The amount of the monomer having a carboxyl group is preferably 65 mol% or less, and more preferably 50 mol% or less. If the amount is 65 mol% or less, the Tg of a coating film to be obtained is not too high with respect to a suitable range to be described later, and film-forming properties and stretching suitability in in-line coating are good, which is preferable.

[0029]

In order to exhibit good water solubility, it is preferable to neutralize the carboxyl group introduced into the acrylic resin by the copolymerization of acrylic acid or methacrylic acid. Examples of basic neutralizing agents include amine compounds such as ammonia, trimethylamine, triethylamine, and dimethylaminoethanol, and inorganic basic substances such as potassium hydroxide and sodium hydroxide. Among these, an amine compound is preferably used as the neutralizing agent for the ease of the volatilization of the neutralizing agent and the ease of the formation of the crosslinked structure. A neutralization rate is preferably 30 mol% to 95 mol%, and more preferably 40 mol% to 90 mol%. When the

neutralization rate is 30 mol% or more, the water solubility of the acrylic resin is sufficient; the acrylic resin is easily dissolved during the preparation of a coating solution; and no blanching of the coating surface after drying may be caused, which is preferable.

Meanwhile, when the neutralization rate is 95 mol% or less, the water solubility is not too high, and alcohol and the like is easily mixed during the preparation of the coating solution, which is preferable.

[0030]

The acid value of the acrylic resin is preferably 40 mgKOH/g or more, more preferably 50 mgKOH/g or more, and still more preferably 60 mgKOH/g or more. If the acid value of the acrylic resin is 40 mgKOH/g or more, the number of crosslinking points with the oxazoline-based cross-linking agent or the carbodiimide-based cross-linking agent increases, whereby a robust coating film having a higher crosslinking density can be obtained, which is preferable.

[0031]

The acid value of the acrylic resin is preferably 400 mgKOH/g or less, more preferably 350 mgKOH/g or less, and still more preferably 300 mgKOH/g or less. If the acid value of the acrylic resin is 400 mgKOH/g or less, the carboxyl group of the acrylic resin and the particles

contained in the easy-to-slip coating layer cause no extreme interaction to provide the uniform dispersion of the particles, which is preferable. If the dispersibility of the particles is good, coarse protrusions do not occur in the easy-to-slip coating surface, and no pinholes occur in a ceramic sheet, which is preferable.

[0032]

The glass transition temperature (T_g) of the acrylic resin is preferably 50°C or higher, more preferably 55°C or higher, and still more preferably 60°C or higher. If the glass transition temperature of the acrylic resin is 50°C or higher, the hardness of the easy-to-slip coating layer becomes moderately high, which is preferable.

[0033]

The glass transition temperature (T_g) of the acrylic resin is preferably 110°C or lower, more preferably 105°C or lower, and still more preferably 100°C or lower. If the glass transition temperature of the acrylic resin is 110°C or lower, uniform stretching is provided without causing cracks to occur in the coating film in a stretching step after the easy-to-slip coating layer is coated, which is preferable.

[0034]

As a T_g adjusting monomer copolymerized to set the T_g to the above range, (meth)acrylic monomers and non-acrylic

vinyl monomers can be utilized. Specific examples of the (meth)acrylic monomers include (meth)acrylic acid alkyl esters such as methyl(meth)acrylate, ethyl(meth)acrylate, isopropyl(meth)acrylate, n-butyl(meth)acrylate, isobutyl(meth)acrylate, n-amyl(meth)acrylate, n-hexyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, n-octyl(meth)acrylate, decyl(meth)acrylate, dodecyl(meth)acrylate, cyclohexyl(meth)acrylate, isobornyl(meth)acrylate, and stearyl(meth)acrylate; nitrogen-containing acrylic monomers such as (meth)acrylamide, diacetone acrylamide, n-methylolacrylamide, and (meth)acrylonitrile; and vinyl methacrylate. One or two or more of the (meth)acrylic monomers can be used.

[0035]

Examples of the non-acrylic vinyl monomers include styrene-based monomers such as styrene, α -methylstyrene, vinyltoluene (a mixture of m-methylstyrene and p-methylstyrene), and chlorostyrene; vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl caproate, vinyl caprylate, vinyl caprate, vinyl laurate, vinyl myristate, vinyl palmitate, vinyl stearate, vinyl cyclohexanecarboxylate, vinyl pivalate, vinyl octylate, vinyl monochloroacetate, divinyl adipate, vinyl crotonate, vinyl sorbate, vinyl benzoate, and vinyl cinnamate; and

vinyl halide monomers such as vinyl chloride and vinylidene chloride. One or two or more of the non-acrylic vinyl monomers can be used.

[0036]

It is preferable that, after the appropriate amounts of a hydroxyl group-containing monomer and a carboxyl group-containing monomer are determined, the Tg adjusting monomer be the remainder. The Tg of the copolymer is determined by the following Fox formula.

[0037]

[Equation 1]

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} + \dots + \frac{W_n}{T_{g_n}}$$

W_n : Mass fraction of each monomer (% by mass)

T_{g_n} : Tg (K) of homopolymer of each monomer

[0038]

A component that lowers surface free energy such as a long-chain alkyl group may be introduced as a monomer copolymerized for Tg adjustment. An acrylic resin into which a long-chain alkyl group is introduced preferably has an alkyl group having about 8 to 20 carbon atoms in its side chain. 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.

[0039]

The amount of the monomer having a long-chain alkyl group in the monomer copolymerized for Tg adjustment is preferably 50 mol% or less, and more preferably 40 mol% or less, in 100 mol% of all constituent units of the acrylic resin. When the amount is 50 mol% or less, the Tg of the coating film to be obtained is not too low with respect to a suitable range, and the hardness of the coating film can be highly maintained, which is preferable. In the present invention, the amount of the monomer having a long-chain alkyl group may be 0 mol% as long as the Tg can be maintained in a suitable range, but if the amount is 5 mol% or more, an effect of adjusting the Tg of the acrylic resin is clear, which is preferable.

[0040]

The acrylic resin used in the present invention can be obtained by known radical polymerization. Any of emulsion polymerization, suspension polymerization, solution polymerization, and bulk polymerization and the like can be employed. From the viewpoint of handleability, the solution polymerization is preferable. Examples of water-soluble organic solvents that can be used for the solution polymerization include ethylene glycol n-butyl

ether, isopropanol, ethanol, n-methylpyrrolidone, tetrahydrofuran, 1,4-dioxane, 1,3-oxolane, methyl cellosolve, ethyl cellosolve, ethyl carbitol, butyl carbitol, propylene glycol monopropyl ether, and propylene glycol monobutyl ether. These may be used in mixture with water.

[0041]

A polymerization initiator may be any known compound that generates radicals, but a water-soluble azo-based polymerization initiator such as 2,2-azobis-2-methyl-N-2-hydroxyethylpropionamide is preferable. The temperature and time and the like of the polymerization are appropriately selected.

[0042]

The mass average molecular weight (M_w) of the acrylic resin is preferably about 10,000 to 200,000. The range of the mass average molecular weight is more preferably 20,000 to 150,000. When the M_w is 10,000 or more, there is no fear of thermal decomposition in a tenter, which is preferable. If the M_w is 200,000 or less, the viscosity of the coating solution does not significantly increase to provide good coating performance, which is preferable.

[0043]

As a binder of the easy-to-slip coating layer in the present invention, other binder resins may be used in

combination in addition to the acrylic resin. Examples of the other binder resins include a polyester resin, an urethane resin, a polyvinyl-based resin (polyvinyl alcohol and the like), polyalkylene glycol, polyalkyleneimine, methylcellulose, hydroxycellulose, and starch.

[0044]

The content of the acrylic resin in the easy-to-slip coating layer is preferably 20% by mass or more and 95% by mass or less in the total solid content. The content is more preferably 30% by mass or more and 90 % by mass or less. If the content is 20% by mass or more, the content of the carboxyl group as a crosslinking component is not too small, whereby the crosslinking density does not decrease, which is preferable. If the content is 95% by mass or less, the amount of the cross-linking agent to be crosslinked is not too small, whereby the crosslinking density does not decrease, which is preferable.

[0045]

(Cross-Linking Agent)

In the present invention, in order to form the crosslinked structure in the easy-to-slip coating layer, the easy-to-slip coating layer preferably contains at least one cross-linking agent selected from an oxazoline-based cross-linking agent or a carbodiimide-based cross-linking agent. The inclusion of the oxazoline-based cross-linking

agent or the carbodiimide-based cross-linking agent provides improvement in adhesion with a PET substrate and promotion of crosslinking with the carboxyl group of the acrylic resin to allow the coating film strength of the easy-to-slip layer to be improved. As a result, unwinding electric charge when the release film roll is unwound can be suppressed. Other cross-linking agents may be used in combination, and specific examples of the cross-linking agents that can be used in combination include urea-based, epoxy-based, melamine-based, isocyanate-based, and silanol-based cross-linking agents. In order to promote a crosslinking reaction, a catalyst and the like can be appropriately used as needed.

[0046]

Examples of the cross-linking agent having an oxazoline group include a polymer having an oxazoline group that is obtained by copolymerizing a polymerizable unsaturated monomer having an oxazoline group and other polymerizable unsaturated monomer as needed by a conventionally known method (for example, solution polymerization or emulsion polymerization or the like).

[0047]

Examples of the polymerizable unsaturated monomer having an oxazoline group include 2-vinyl-2-oxazoline, 2-vinyl-4-methyl-2-oxazoline, 2-vinyl-5-methyl-2-oxazoline,

2-isopropenyl-2-oxazoline, 2-isopropenyl-4-methyl-2-oxazoline, and 2-isopropenyl-5-ethyl-2-oxazoline. These monomers may be used alone or in combination of two or more thereof.

[0048]

Examples of the other polymerizable unsaturated monomer include alkyl or cycloalkyl esters of (meth)acrylic acid that each have 1 to 24 carbon atoms such as methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, cyclohexyl(meth)acrylate, lauryl(meth)acrylate, and isobornyl(meth)acrylate; hydroxyalkyl esters of (meth)acrylic acid that each have 2 to 8 carbon atoms such as 2-hydroxyethyl(meth)acrylate and hydroxypropyl(meth)acrylate; vinyl aromatic compounds such as styrene and vinyltoluene; (meth)acrylamide, dimethylaminopropyl(meth)acrylamide, dimethylaminoethyl(meth)acrylate, and any adduct of glycidyl(meth)acrylate and an amine; polyethylene glycol(meth)acrylate; and N-vinylpyrrolidone, ethylene, butadiene, chloroprene, vinyl propionate, vinyl acetate, and (meth)acrylonitrile. These monomers may be used alone or in combination of two or more thereof.

[0049]

In order to render the obtained cross-linking agent

having an oxazoline group a water-soluble cross-linking agent, the other polymerizable unsaturated monomer is preferably a hydrophilic monomer from the viewpoint of improvements in compatibility with other resins, wettability, and crosslinking reaction efficiency and the like. Examples of the hydrophilic monomer include 2-hydroxyethyl(meth)acrylate, methoxy polyethylene glycol(meth)acrylate, monomers each having a polyethylene glycol chain, such as a monoester compound made of (meth)acrylic acid and polyethylene glycol, 2-aminoethyl(meth)acrylate and salts thereof, (meth)acrylamide, N-methylol(meth)acrylamide, N-(2-hydroxyethyl)(meth)acrylamide, (meth)acrylonitrile, and sodium styrenesulfonate. Among these, preferred are methoxy polyethylene glycol(meth)acrylate, and monomers each having a polyethylene glycol chain, such as a monoester compound made of (meth)acrylic acid and polyethylene glycol, which have a high solubility in water.

[0050]

The cross-linking agent having an oxazoline group preferably has an oxazoline group content of 3.0 to 9.0 mmol/g. More preferably, the oxazoline group content is in a range of 4.0 to 8.0 mmol/g. If the oxazoline group content is in the range of 4.0 to 8.0 mmol/g, an appropriate crosslinked structure can be formed, which is

preferable.

[0051]

Examples of the carbodiimide-based cross-linking agent include a monocarbodiimide compound and a polycarbodiimide compound. Examples of the monocarbodiimide compound include dicyclohexylcarbodiimide, diisopropylcarbodiimide, dimethylcarbodiimide, diisobutylcarbodiimide, dioctylcarbodiimide, t-butylisopropylcarbodiimide, diphenylcarbodiimide, di-t-butylcarbodiimide, and di- β -naphthylcarbodiimide. As the polycarbodiimide compound, polycarbodiimide compounds produced by a conventionally known method can be used. For example, the polycarbodiimide compound can be produced by synthesizing an isocyanate terminate polycarbodiimide in a condensation reaction involving decarboxylation of diisocyanate.

[0052]

Examples of the diisocyanate that is the synthetic raw material of the polycarbodiimide compound include isomers of toluylene diisocyanate, aromatic diisocyanates such as 4,4-diphenylmethane diisocyanate, aromatic aliphatic diisocyanates such as xylylene diisocyanate, alicyclic diisocyanates such as isophorone diisocyanate and 4,4-dicyclohexylmethane diisocyanate and 1,3-bis(isocyanatomethyl)cyclohexane, and aliphatic

diisocyanates such as hexamethylene diisocyanate and 2,2,4-trimethylhexamethylene diisocyanate. From the problem of yellowing, the aromatic aliphatic diisocyanates, the alicyclic diisocyanates, and the aliphatic diisocyanates are preferable.

[0053]

The diisocyanate may be used with molecules controlled to an appropriate degree of polymerization using a compound that reacts with a terminal isocyanate such as monoisocyanate. Examples of the monoisocyanate for sealing the terminals of the polycarbodiimide to control the degree of polymerization thereof include phenyl isocyanate, toluylene isocyanate, dimethylphenyl isocyanate, cyclohexyl isocyanate, butyl isocyanate, and naphthyl isocyanate. In addition, a compound having an OH group, -NH₂ group, a COOH group, or a SO₃H group can be used as a terminal sealing agent.

[0054]

The condensation reaction involving decarboxylation of diisocyanate proceeds in the presence of a carbodiimidization catalyst. Examples of the catalyst include phospholene oxides such as 1-phenyl-2-phospholene-1-oxide, 3-methyl-2-phospholene-1-oxide, 1-ethyl-2-phospholene-1-oxide, 3-methyl-1-phenyl-2-phosphorene-1-oxide, and 3-phospholene isomers of these, and 3-methyl-1-

phenyl-2-phospholene-1-oxide is preferable from the viewpoint of reactivity. The amount of the catalyst used may be a catalyst amount.

[0055]

The mono or polycarbodiimide compound described above is desirably kept in a uniform dispersed state when blended with an aqueous coating material. For this purpose, the mono or polycarbodiimide compound emulsified with an appropriate emulsifier is preferably used as an emulsion, or blended with a coating material in the form of a self-emulsified product or in the form of a self-dissolved product by adding a hydrophilic segment into the molecular structure of the polycarbodiimide compound.

[0056]

Examples of the carbodiimide-based cross-linking agent used in the present invention include water-dispersible and water-soluble carbodiimide-based cross-linking agents. The water-soluble carbodiimide-based cross-linking agent is preferable since the cross-linking agent has good compatibility with other water-soluble resins and improves the crosslinking reaction efficiency of the easy-to-slip coating layer. The water-soluble carbodiimide compound can be produced by synthesizing an isocyanate terminate polycarbodiimide in a condensation reaction involving decarboxylation of isocyanate, and

thereafter adding a hydrophilic moiety having a functional group having reactivity with an isocyanate group.

[0057]

Examples of the hydrophilic moiety include (1) quaternary ammonium salts of dialkylamino alcohols and quaternary ammonium salts of dialkylaminoalkylamines, and the like, (2) alkyl sulfonates having at least one reactive hydroxyl group, and the like, and (3) poly(ethylene oxide) terminal-sealed with an alkoxy group, and a mixture of poly(ethylene oxide) and poly(propylene oxide). The carbodiimide compound becomes (1) cationic, (2) anionic, and (3) nonionic when the hydrophilic moiety is introduced. Among these, nonionic compounds having compatibility with other water-soluble resin, regardless of the ionicity of the resin, is preferable.

[0058]

The content of the cross-linking agent in the easy-to-slip coating layer is preferably 5% by mass or more and 80% by mass or less in the total solid content. The content is more preferably 10% by mass or more and 70% by mass or less. If the content is 5% by mass or more, the crosslinking density of the resin of the coating layer does not decrease, which is preferable. If the content is 80 % by mass or less, the amount of the carboxyl groups of the acrylic resin to be crosslinked is not too small, whereby

the crosslinking density does not decrease, which is preferable.

[0059]

(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) acrylic or methacrylic, vinyl chloride-based, vinyl acetate-based, nylon, styrene/acrylic, styrene/butadiene-based, polystyrene/acrylic, 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.

[0060]

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.

[0061]

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.

[0062]

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 (RSm) of a roughness curve element 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.

[0063]

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.

[0064]

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 indefinite shape can be used. The average particle size of the particles having an indefinite 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.

[0065]

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.

[0066]

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.

[0067]

As a method for measuring the content rate of particles contained in an 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, an 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.

[0068]

(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.

[0069]

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.

[0070]

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.

[0071]

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.

[0072]

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 mixed with a water-soluble organic solvent from the viewpoint of environmental issues.

[0073]

The concentration of the solid content 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.

[0074]

A drying temperature after coating is also preferably 70°C or higher, and preferably 250°C or lower 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.

[0075]

(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, extruding it into a sheet shape, stretching an obtained non-oriented polyester sheet 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.

[0076]

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.

[0077]

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.

[0078]

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.

[0079]

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.

[0080]

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 are maintained to provide a uniform coating film, which is preferable.

[0081]

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.

[0082]

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) be 1 nm or more and 25 nm or less, and a maximum protrusion height (P) be 60 nm or more and 500 nm or less.

[0083]

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 (S_a) 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.

[0084]

In the present invention, it is preferable that the average area surface roughness (S_a) and the maximum protrusion height (P) are set within the above ranges, and an average length (R_{Sm}) of a roughness curve element is 10

μm or less. By controlling the average length (R_{Sm}) of the roughness curve element to $10\ \mu\text{m}$ 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 (R_{Sm}) of the roughness curve element is more preferably $5\ \mu\text{m}$ or less, and still more preferably $3\ \mu\text{m}$ or less. However, the too small average length (R_{Sm}) of the roughness curve element 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 (S_a) and an increase in the maximum protrusion height (P). The average length (R_{Sm}) of the roughness curve element is preferably $0.1\ \mu\text{m}$ or more, may be $0.5\ \mu\text{m}$ or more, and may be $1\ \mu\text{m}$ or more.

[0085]

In the present invention, in order to set the average length (R_{Sm}) of the roughness curve element within a predetermined range, the average particle size of the particles contained in the easy-to-slip coating layer is preferably $1000\ \text{nm}$ or less. The average particle size is more preferably $800\ \text{nm}$ or less, and more preferably $600\ \text{nm}$ or less. If the average particle size is $1000\ \text{nm}$ or less,

the distance between the particles does not become too large, and the average length R_{Sm} is adjusted to a predetermined range, which is preferable.

[0086]

(Release Coating Layer)

A resin constituting the release coating layer in the present invention is not particularly limited, and a silicone resin, a fluorine resin, an alkyd resin, various waxes, and an aliphatic olefin and the like can be used. The resins may be used alone or in combination of two or more thereof.

[0087]

In the release coating layer in the present invention, for example, the silicone resin is a resin having a silicone structure in its molecule, and examples thereof include modified silicone resins such as curing type silicone, a silicone graft resin, and an alkyl modified resin. It is preferable to use a reactive curable silicone resin from the viewpoint of transitivity and the like. As the reactive curable silicone resin, an addition reaction type, condensation reaction type, ultraviolet ray, or electron beam curing type reactive curable silicone resin or the like can be used. A low-temperature curable addition reaction type reactive curable silicone resin that can be processed at a low temperature, and an ultraviolet

ray or electron beam curing type reactive curable silicone resin are more preferable. These materials to be used can be processed at a low temperature during the coating processing of the materials to the polyester film. Therefore, a polyester film having high flatness can be obtained with less thermal damage to the polyester film during processing, and defects such as pinholes can be reduced even when a super-thin layer ceramic green sheet having a thickness of 0.2 to 2.0 μm is produced.

[0088]

Examples of the addition reaction type silicone resin include an addition reaction type silicone resin obtained by reacting polydimethylsiloxane having a vinyl group introduced into a terminal or side chain thereof with hydrodienesiloxane using a platinum catalyst, and curing the reaction product. At this time, the use of a resin that can be cured at 120°C within 30 seconds can provide processing at a low temperature, which is more preferable. Examples of thereof include low-temperature addition curing type (LTC1006L, LTC1056L, LTC300B, LTC303E, LTC310, LTC314, LTC350G, LTC450A, LTC371G, LTC750A, LTC755, and LTC760A, and the like) and thermal UV curing type (LTC851, BY24-510, BY24-561, and BY24-562, and the like) silicone resins, manufactured by Dow Corning Toray Co., Ltd., and solvent addition + UV curing type (X62-5040, X62-5065, X62-5072T,

and KS5508 and the like) and dual curing type (X62-2835, X62-2834, and X62-1980, and the like) silicone resins, manufactured by Shin-Etsu Chemical Co., Ltd.

[0089]

Examples of the condensation reaction type silicone resin include a condensation reaction type silicone resin in which a polydimethylsiloxane having an OH group at its terminal and a polydimethylsiloxane having an H group at its terminal are subjected to a condensation reaction using an organotin catalyst to form a three-dimensional crosslinked structure.

[0090]

Examples of the ultraviolet curing type silicone resin include an ultraviolet curing type silicone resin that utilizes the same radical reaction as that of ordinary silicone rubber crosslink as the most basic type, an ultraviolet curing type silicone resin that is obtained by introducing an unsaturated group, followed by photo-curing, an ultraviolet curing type silicone resin that is obtained by decomposing an onium salt with ultraviolet light to generate a strong acid and causing the strong acid to cleave an epoxy group for crosslinking, and an ultraviolet curing type silicone resin that is crosslinked by the addition reaction of thiol to vinylsiloxane. An electron beam can be used in place of the ultraviolet light. The

electron beam has stronger energy than that of the ultraviolet light, and can provide a radical crosslinking reaction without using an initiator as in the case of ultraviolet curing. Examples of the resin to be used include UV curing type silicones, manufactured by Shin-Etsu Chemical Co., Ltd. (X62-7028A/B, X62-7052, X62-7205, X62-7622, X62-7629, and X62-7660 and the like), UV curing type silicones, manufactured by Momentive Performance Materials (TPR6502, TPR6501, TPR6500, UV9300, UV9315, XS56-A2982, and UV9430 and the like), and UV curing type silicones (Silcoleases UV POLY200, POLY215, POLY201, and KF-UV265AM and the like), manufactured by Arakawa Chemical Industries, Ltd.

[0091]

As the ultraviolet curing type silicone resin, polydimethylsiloxane modified with acrylate or glycidoxo, or the like may also be used. By mixing the modified polydimethylsiloxane with a polyfunctional acrylate resin or an epoxy resin or the like, and using the mixture in the presence of an initiator, good release performance can also be provided.

[0092]

As other examples of the resin to be used, an alkyd resin and an acrylic resin that are modified with stearyl and lauryl and the like, an alkyd-based resin that is

obtained by the reaction of methylated melamine and the like, or an acrylic resin or the like is also suitable.

[0093]

Examples of an aminoalkyd resin obtained by the reaction of methylated melamine and the like include Tesfine 303, Tesfine 305, and Tesfine 314, manufactured by Hitachi Chemical Co., Ltd. Examples of an aminoacrylic resin obtained by the reaction of methylated melamine and the like include Tesfine 322, manufactured by Hitachi Chemical Co., Ltd.

[0094]

When the resins are used for the release coating layer in the present invention, the resins may be used alone or in combination of two or more thereof. In order to adjust a peeling force, it is also possible to mix an additive such as a light peeling additive or a heavy peeling additive.

[0095]

The release coating layer in the present invention can contain particles having a particle size of 1 μm or less, but it is preferable that the release coating layer substantially contains no component forming projections such as particles from the viewpoint of the occurrence of the pinholes.

[0096]

Additives such as an adhesion improver and an anti-static agent may be added to the release coating layer in the present invention. 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.

[0097]

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 thickness of the release coating layer after curing is preferably 0.005 to 2.0 μm . If the thickness of the release coating layer is 0.005 μm or more, the release performance is maintained, which is preferable. If the thickness of the release coating layer is 2.0 μm or less, a curing time does not become too long, whereby the uneven thickness of the ceramic green sheet due to a decrease in the flatness of the release film may not occur, which is preferable. Since the curing time does not become too long, the resin constituting the release coating layer may not aggregate, and the protrusions may not be formed, whereby the defects of the pinholes of the ceramic green sheet are less likely to occur, which is preferable.

[0098]

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.

[0099]

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.

[0100]

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 release 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, heat curing, or ultraviolet curing. At this time, a drying temperature during solvent drying and thermosetting is preferably 180°C or lower, more preferably 150°C or lower, and most preferably 120°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 120°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.

[0101]

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.

[0102]

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.

[0103]

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.

[0104]

(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.

[0105]

The release film for producing a ceramic green sheet of the present invention is used for producing such a multilayer ceramic capacitor. For example, the release film for producing 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

[0106]

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.

[0107]

[NMR Measurement]

The ratio of a copolymer component introduced into an acrylic polyol was confirmed by nuclear magnetic resonance spectrometry (^1H -NMR, ^{13}C -NMR: Varian Unity 400, manufactured by Agilent Technologies). The measurement was carried out by removing a solvent in the synthesized acrylic polyol with a vacuum dryer and then dissolving the dried product in deuterated chloroform. From the obtained NMR spectrum, the peaks of chemical shifts δ (ppm) attributed to the moieties of groups were identified. The integrated intensity of each of the obtained peaks was obtained, and the composition ratio (mol%) of the copolymer component introduced into the acrylic polyol was confirmed from the number of hydrogens and integrated intensity of the moiety of each group.

[0108]

[Confirmation of Tg]

The Tg of each acrylic polyol was obtained from the composition ratio of the copolymer component obtained in the NMR measurement and the above-described Fox formula.

[0109]

[Stretching Adequacy]

In order to evaluate the stretching adequacy of the acrylic polyol itself, the synthesized acrylic polyols (1) to (12) were charged into a mixed solvent (25°C) of 30% by mass of isopropanol and 70% by mass of water such that the solid content concentration was 12% by mass, to prepare a solution containing the acrylic polyol alone. Then, the solution was coated on the surface of the polyester film subjected to only longitudinal stretching with Mayer bar #5. Then, a film sample on which the coating layer (thickness: 6.5 μm) has been formed was allowed to stand in a hot air circulating oven set at a temperature of 60°C for 30 seconds. Then, the film sample was taken out of the oven, and pre-dried. Then, the sample was set in a hand-turned stretching apparatus (manufactured by Toyobo Engineering Co., Ltd.). The stretching apparatus was placed in a hot air circulation oven at 100°C to slowly stretch the sample. The sample was stretched until the length was 4 times the length of the sample before stretching, and the stretching apparatus was taken out from the hot air circulation oven. Thereafter, the stretched

coating film was observed with an optical microscope (magnification: 200 times), and the presence or absence of cracking due to stretching was determined according to the following criteria.

Good: No cracks are observed.

Average: Some cracks are observed (1 to 4).

Poor: 5 or more cracks, or cracks are observed in the entire surface.

[0110]

(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 (S_a) and an average length (R_{Sm}) of a roughness curve element, 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 $187 \times 139 \mu\text{m}$ (S_a , P measurement)
- Measurement length (L_r : reference length): $187 \mu\text{m}$

(R_{Sm} measurement)

[0111]

(2) Evaluation of Dispersibility of Particles of Easy-To-Slip Coating Layer

The maximum protrusion height (P) value measured in (1) above was used for determination based on the following criteria.

Good: The maximum protrusion height (P) is 0.2 μm or less.

Good Average: The maximum protrusion height (P) is larger than 0.2 μm and smaller than 0.3 μm .

Average: The maximum protrusion height (P) is 0.3 μm or more.

[0112]

(3) Measurement of Martens Hardness and Ratio of Elastic to Total Work of single film of a mixture composition comprising a resin and a cross-linking agent both used in Easy-To-Slip Coating Layer

The solid content concentration of a mixture composition comprising a resin and a cross-linking agent as a sample was adjusted to 12% by mass by a mixed solvent (25°C) of 30% by mass of isopropanol and 70% by mass of water. The solution was coated on the surface of a slide glass with Mayer bar #28. Then, a slide glass sample on which the coating layer (thickness: 5.0 μm) has been formed was allowed to stand in a hot air circulating oven set at a

temperature of 80°C for 5 minutes. Then, the film sample was taken out of the oven, and pre-dried. Then, the sample was allowed to stand in a hot air circulating oven set at a temperature of 230°C for 2 minutes, and the film sample was then taken out of the oven for a heat treatment.

The surface of the obtained sample piece was subjected to a load-unload test using a dynamic ultra-fine hardness tester (DUH-211S, manufactured by Shimadzu Corporation). From this measurement, the Martens hardness (HM) and the ratio of elastic to total work (η_{it}) were determined using the following equations (average value of $n=10$).

$$HM = F / (26.43 \times h^2) (N/mm^2)$$

(F: load (N), h: pressing depth (mm))

$$W_{total} = W_{plast} + W_{elast} (N \cdot m)$$

(W_{total} = total deformation work (N·m), W_{plast} = plastic deformation work (N·m), W_{elast} = elastic deformation work (N·m))

$$\eta_{it} = (W_{elast} / W_{plast}) \times 100 (\%)$$

(Measurement Conditions)

- (1) Indenter used: Diamond triangular pyramid indenter (angle between ridges: 115°)
- (2) Measurement mode: load-unload test
- (3) Testing force: 0.5 mN
- (4) Minimum test force: 0.002 mN

- (5) Load speed: 0.025 mN/sec
- (6) Load holding time: 2 sec
- (7) Unload hold time: 0 sec
- (8) Measurement atmosphere: 25 $\pm$ 1°C, 65 $\pm$ 5% RH
- (9) Measurement n number: 10

[0113]

(4) Unwinding Electric Charge of Roll of Release Film

The release film for producing the green sheet obtained in each of Examples and Comparative Examples was wound in a roll shape with a width of 400 mm and a length of 5000 m to obtain a roll of the release film. The roll of the release film was stored at a temperature of 40°C and at a humidity of 50% or less for 30 days. Thereafter, an electric charge amount when the release film was unwound at a speed of 100 m/min was measured using "KSD-0103", manufactured by KASUGA ELECTRIC WORKS LTD. The electric charge amount was measured in a region of 100 mm of the just-unwound release film every an unwinding length of 500 M, and the average value thereof was calculated.

Good: less than $\pm$ 3 kV

Good Average: $\pm$ 3 kV or more and less than 5 kV

Average: $\pm$ 5 kV or more and less than 10 kV

Poor: $\pm$ 10 kV or more

[0114]

(5) 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 μm , 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 weight of 1 kg/cm² 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.

Average: Occurrence of pinholes is very slight, and thickness variation is slightly observed.

Poor: Occurrence of pinholes is slight, and thickness variation is slightly conspicuous.

[0115]

(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 a 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 obtained by sintering stainless steel fibers having a 95% cut diameter of 20 μm , 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.

[0116]

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

Meanwhile, in the above 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)).

[0117]

(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 obtained by sintering stainless steel fibers having a 95% cut diameter of 15 μm and a filter obtained by sintering stainless steel particles having a 95% cut diameter of 15 μm , and merged in a feed block. The PET (I) and the PET (II) were laminated

such that the PET (I) was an opposite side layer to a release surface and the PET (II) was a release surface side layer, 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 side layer to a release surface was 28 nm.

[0118]

(Production of Acrylic Polyol A-1)

77 parts by mass of methyl methacrylate (MMA), 100

parts by mass of hydroxyethyl methacrylate (HEMA), 33 parts by mass of methacrylic acid (MAA), and 490 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-hydroxyethylpropionamide 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. 840 parts by mass of an IPA aqueous solution (water content: 50% by mass) was added and mixed. 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-1) having a solid content concentration of 20% by mass. The composition ratio, T_g, stretching adequacy, and acid value

of the acrylic polyol (A-1) as measured by NMR were also shown in Table 1.

[0119]

(Production of Acrylic Polyols (A-2) to (A-12))

As shown in Table 1, acrylic polyols (A-2) to (A-12) having a solid content concentration of 20% by mass were obtained in the same manner as in the production of the acrylic polyol 1 except that MMA, St, SMA, HEMA, MAA, AA, IPA during charging, and the amount of the IPA aqueous solution during dilution were changed. The composition ratio, Tg, stretching adequacy, and acid value of each of the acrylic polyols (A-2) to (A-12) as measured by NMR were also shown in Table 1. The composition ratio was represented with MMA, St (styrene), SMA (stearyl methacrylate) as l-1, l-2, l-3 (unit), HEMA as m (unit), and MAA and AA (acrylic acid) as n (unit).

[0120]

[Table 1]

Number	Acrylic polyol										Solvent				Composition ratio in acrylic resin (mol%)					Various physical properties		
	l-1		l-2		l-3		m		n		During polymerization		During dilution									
	Material	Parts to be charged (parts by mass)	Material	Parts to be charged (parts by mass)	Material	Parts to be charged (parts by mass)	Material	Parts to be charged (parts by mass)	Material	Parts to be charged (parts by mass)	Material	Parts to be charged (parts by mass)	Material	Parts to be charged (parts by mass)	l-1	l-2	l-3	m	n	Tg (°C)	Stretching adequacy	Acid value (mgKOH /g)
A-1	MMA	77	St	0	SMA	0	HEMA	100	MAA	33	IPA	490	IPA aqueous solution	840	40	0	0	40	20	86	Good	205
A-2		103		0		0		100		66		627		1075	40	0	0	30	30	100	Good	321
A-3		58		0		0		100		50		484		829	30	0	0	40	30	92	Good	312
A-4		38		0		0		100		11		349		598	30	0	0	60	10	66	Good	96
A-5		5		0		0		100		3		252		432	6	0	0	90	4	45	Good	35
A-6		58		0		0		100		215		869		1490	15	0	0	20	65	133	Average	752
A-7		77		0		0		100		132		721		1237	25	0	0	25	50	118	Average	558
A-8		58		20		0		100		33		492		843	30	10	0	40	20	86	Good	205
A-9		0		0		260		100		33		918		1573	0	0	40	40	20	59	Good	110
A-10		231		0		130		100		33		1153		1976	60	0	10	20	10	88	Good	87
A-11		103		0		173		100		22		929		1592	40	0	20	30	10	73	Good	72
A-12		77		0		0		100	AA	28		477		819	40	0	0	40	20	75	Good	211

MMA Methyl methacrylate
 St Styrene
 SMA Stearyl methacrylate
 HEMA Hydroxyethyl methacrylate
 MAA Methacrylic acid
 AA Acrylic acid

[0121]

(Polymerization of Polyester Resin B0-1)

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 (B0-1). The obtained copolymerized polyester resin (B0-1) was light yellow and transparent. The reduced viscosity of the copolymerized polyester resin (B0-1) was measured, and found to be 0.60 dl/g. The glass transition temperature by DSC was 65°C.

[0122]

(Production of Polyester Water Dispersion B-1)

30 parts by mass of a polyester resin (B0-1) 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 (B-1) having a solid content of 30% by mass.

[0123]

(Polymerization of Polyester Resin B0-2)

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 (B0-2). The obtained hydrophobic copolymerized polyester resin (B0-2) was light yellow and transparent.

[0124]

(Production of Polyester Water Dispersion B-2)

Then, 60 parts by mass of the copolymerized polyester resin (B0-2), 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 light yellow transparent polyester-based resin. A uniform water-dispersible polyester-based graft copolymer dispersion solution (B-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.

[0125]

(Polyester Water dispersion B-3)

Vylonal (registered trademark) MD1500, manufactured by TOYOB0 CO., LTD., Tg = 77°C, solid content concentration: 30% by mass) was used.

[0126]

(Production of Polyurethane Water Dispersion C-1)

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 C-1 having a solid content of 37% by mass. The glass transition temperature of the obtained polyurethane resin was -30°C.

[0127]

(Production of Oxazoline-Based Cross-Linking Agent D-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 (D-1) having a solid content concentration of 25% and having an oxazoline group. The oxazoline group amount of the obtained resin (D -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.

[0128]

(Production of Oxazoline-Based Cross-Linking Agent D-2)

A resin (D-2) having a different composition (oxazoline group amount and molecular weight), having a solid content concentration of 10%, and having an oxazoline group was obtained in the same manner as in the synthesis of the resin (D-1) having an oxazoline group. The obtained resin (D-2) having an oxazoline group had an oxazoline group amount of 7.7 mmol/g, and the number-average molecular weight thereof measured by GPC was 40,000.

[0129]

(Production of Carbodiimide-Based Cross-Linking Agent E-1)

168 parts by mass of hexamethylene diisocyanate and 220 parts by mass of polyethylene glycol monomethyl ether (M400, average molecular weight: 400) were charged into a flask equipped with a stirrer, a thermometer, and a reflux condenser, and stirred at 120°C for 1 hour. Furthermore, 26 parts by mass of 4,4'-dicyclohexylmethane diisocyanate and 3.8 parts by mass of 3-methyl-1-phenyl-2-phospholene-1-oxide (2% by mass based on the total isocyanate) as a carbodiimidization catalyst were added thereto, followed by stirring at 185°C under nitrogen flow for another 5 hours. The infrared spectrum of the reaction solution was measured, and the absorption at a wavelength of 2200 to 2300 cm^{-1} was confirmed to disappear. The mixture was allowed to cool to 60°C, and 567 parts by mass of ion-exchanged water was added thereto to obtain a carbodiimide water-soluble resin (E-1) having a solid content of 40% by mass.

[0130]

(Production of Isocyanate Cross-Linking Agent F-1)

100 parts by mass of a polyisocyanate compound obtained from using hexamethylene diisocyanate as a raw material and having an isocyanurate structure (Duranate TPA, manufactured by Asahi Kasei Chemicals), 55 parts by mass of propylene glycol monomethyl ether acetate, and 30 parts by mass of polyethylene glycol monomethyl ether

(average molecular weight: 750) were charged into a flask equipped with a stirrer, a thermometer, and a reflux condenser, and kept under a nitrogen atmosphere at 70°C for 4 hours. Thereafter, the reaction solution temperature was lowered to 50°C, and 47 parts by mass of methyl ethyl ketoxime was added dropwise. The infrared spectrum of the reaction solution was measured, and the absorption of the isocyanate group was confirmed to disappear. A block polyisocyanate water dispersion solution (F-1) having a solid content of 75% by mass was obtained.

[0131]

(Silica Particle G-1)

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

[0132]

(Silica Particle G-2)

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

[0133]

(Silica Particle G-3)

Colloidal silica (trade name: Snowtex ZL, manufactured by Nissan Chemical Corporation, average

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

[0134]

(Silica Particle G-4)

Colloidal silica (trade name: MP4540M, manufactured by Nissan Chemical Corporation, average particle size: 450 nm, solid content concentration: 40% by mass)

[0135]

(Acrylic Particle G-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)

[0136]

(Release Agent Solution X-1)

100 parts by mass of a thermosetting type amino alkyd resin (Tesfine 314, manufactured by Hitachi Chemical Co., Ltd., solid content: 60% by mass) and 1.2 parts by mass of p-toluenesulfonic acid (Dryer 900, manufactured by Hitachi Chemical Co., Ltd., solid content: 50% by mass) as a curing catalyst were diluted with a toluene/methyl ethyl ketone/heptane (= 3 : 5 : 2) solution to prepare a release agent solution having a solid content of 2% by mass.

[0137]

(Release Agent Solution X-2)

100 parts by mass of a UV curing type silicone resin (UV9300, manufactured by Momentive, solid content concentration: 100% by mass) and 1 part by mass of bis(alkylphenyl)iodonium hexafluoroantimonate as a curing catalyst were diluted with a toluene/methyl ethyl ketone/heptane (= 3 : 5 : 2) solution to prepare a release agent solution having a solid content of 2% by mass.

[0138]

(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: 41.86 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Acrylic polyol resin A-1: 16.57 parts by mass

(Solid content concentration: 20% by mass)

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

Silica particle G-1: 0.59 parts by mass

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

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

[0139]

(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 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.

[0140]

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.

[0141]

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 relaxation 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 .

[0142]

(Formation of Release Coating Layer)

A release agent solution X-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 0.1 μm . Then, the release agent solution was dried with hot air at 130°C for 30 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. The release film for producing a super-thin layer ceramic green sheet had low unwinding electric charge when being wound up as a roll, and then unwound for ceramic sheet coating again and made it possible to suppress the adhesion of environmental foreign matters, whereby a high-quality ceramic capacitor could be prepared without

reducing the yield of the ceramic capacitor.

[0143]

(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 an easy-to-slip coating solution 2 was used, which was obtained by changing the cross-linking agent in the easy-to-slip coating solution 1 used in Example 1 to a carbodiimide-based cross-linking agent E-1 (solid content concentration: 40% by mass).

(Easy-to-slip coating solution 2)

Water: 43.99 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Acrylic polyol resin A-1: 16.57 parts by mass

(Solid content concentration: 20% by mass)

Carbodiimide-based cross-linking agent E-1: 3.55 parts by mass

(Solid concentration: 40% by mass)

Silica particle G-1: 0.59 parts by mass

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

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

[0144]

(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 an easy-to-slip coating solution 3 was used, which was obtained by changing the cross-linking agent in the easy-to-slip coating solution 1 used in Example 1 to an oxazoline-based cross-linking agent D-2 (solid content concentration: 10% by mass).

(Easy-to-slip coating solution 3)

Water: 33.34 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Acrylic polyol resin A-1: 16.57 parts by mass

(Solid content concentration: 20% by mass)

Oxazoline-based cross-linking agent D-2: 14.20 parts by mass

(Solid content concentration: 10% by mass)

Silica particle G-1: 0.59 parts by mass

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

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

[0145]

(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: 43.28 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Acrylic polyol resin A-1: 9.47 parts by mass

(Solid content concentration: 20% by mass)

Oxazoline-based cross-linking agent D-1: 11.36 parts by mass

(Solid content concentration: 25% by mass)

Silica particle G-1: 0.59 parts by mass

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

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

[0146]

(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: 41.15 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Acrylic polyol resin A-1: 20.12 parts by mass
(Solid content concentration: 20% by mass)

Oxazoline-based cross-linking agent

D-1 (Solid content concentration: 25% by mass): 2.84
parts by mass

Silica particle G-1: 0.59 parts by mass
(Average particle size: 200 nm, solid content
concentration: 40% by mass)

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

[0147]

(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 acrylic polyol A-1 (solid content
concentration: 20% by mass) in the easy-to-slip coating
solution 1 used in Example 1 was changed to an acrylic
polyol A-2 (solid content concentration: 20% by mass).

[0148]

(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 acrylic polyol A-1 (solid content
concentration: 20% by mass) in the easy-to-slip coating
solution 1 used in Example 1 was changed to an acrylic

polyol A-3 (solid content concentration: 20% by mass).

[0149]

(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 acrylic polyol A-1 (solid content concentration: 20% by mass) in the easy-to-slip coating solution 1 used in Example 1 was changed to an acrylic polyol A-4 (solid content concentration: 20% by mass).

[0150]

(Example 9)

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 acrylic polyol A-1 (solid content concentration: 20% by mass) in the easy-to-slip coating solution 1 used in Example 1 was changed to an acrylic polyol A-5 (solid content concentration: 20% by mass).

[0151]

(Example 10)

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 acrylic polyol A-1 (solid content concentration: 20% by mass) in the easy-to-slip coating solution 1 used in Example 1 was changed to an acrylic polyol A-6 (solid content concentration: 20% by mass).

[0152]

(Example 11)

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 acrylic polyol A-1 (solid content concentration: 20% by mass) in the easy-to-slip coating solution 1 used in Example 1 was changed to an acrylic polyol A-7 (solid content concentration: 20% by mass).

[0153]

(Example 12)

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 acrylic polyol A-1 (solid content concentration: 20% by mass) in the easy-to-slip coating solution 1 used in Example 1 was changed to an acrylic polyol A-8 (solid content concentration: 20% by mass).

[0154]

(Example 13)

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 acrylic polyol A-1 (solid content concentration: 20% by mass) in the easy-to-slip coating solution 1 used in Example 1 was changed to an acrylic polyol A-9 (solid content concentration: 20% by mass).

[0155]

(Example 14)

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 acrylic polyol A-1 (solid content concentration: 20% by mass) in the easy-to-slip coating solution 1 used in Example 1 was changed to an acrylic polyol A-10 (solid content concentration: 20% by mass).

[0156]

(Example 15)

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 acrylic polyol A-1 (solid content concentration: 20% by mass) in the easy-to-slip coating solution 1 used in Example 1 was changed to an acrylic polyol A-11 (solid content concentration: 20% by mass).

[0157]

(Example 16)

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 acrylic polyol A-1 (solid content concentration: 20% by mass) in the easy-to-slip coating solution 1 used in Example 1 was changed to an acrylic polyol A-12 (solid content concentration: 20% by mass).

[0158]

(Example 17)

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 17.

(Easy-to-slip coating solution 17)

Water: 41.74 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Acrylic polyol resin A-10: 16.57 parts by mass

(Solid content concentration: 20% by mass)

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

Silica particle G-1: 0.59 parts by mass

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

Silica particle G-4: 0.12 parts by mass

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

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

[0159]

(Example 18)

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 18.

(Easy-to-slip coating solution 18)

Water: 41.15 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Acrylic polyol resin A-10: 16.57 parts by mass

(Solid content concentration: 20% by mass)

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

Silica particle G-2: 1.18 parts by mass

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

Silica particle G-4: 0.12 parts by mass

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

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

[0160]

(Example 19)

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 19.

(Easy-to-slip coating solution 19)

Water: 41.27 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Acrylic polyol resin A-10: 16.57 parts by mass

(Solid content concentration: 20% by mass)

Oxazoline-based cross-linking agent D-1: 5.68 parts
by mass

(Solid content concentration: 25% by mass)

Silica particle G-3: 1.18 parts by mass

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

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

[0161]

(Example 20)

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
20.

(Easy-to-slip coating solution 20)

Water: 40.09 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Acrylic polyol resin A-10: 16.57 parts by mass

(Solid content concentration: 20% by mass)

Oxazoline-based cross-linking agent D-1 (Solid

content concentration: 25% by mass): 5.68 parts by mass

Acrylic particle G-5: 2.37 parts by mass

(Average particle size: 150 nm, solid content concentration: 10% by mass)

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

[0162]

(Example 21)

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 release coating layer was formed as follows.

(Formation of Release Coating Layer)

A release agent solution X-2 was coated on an obtained in-line coating polyester film with a reverse gravure coater such that a thickness after drying was 0.1 μm , then dried with hot air at 90°C for 30 seconds, and immediately subjected to ultraviolet irradiation (300 mJ/cm^2) with an electrodeless lamp (H bulb, manufactured by Fusion Co., Ltd.) to form a release coating layer, thereby obtaining a release film for producing a super-thin layer ceramic green sheet.

[0163]

(Example 22)

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 21.

(Easy-to-slip coating solution 21)

Water: 47.39 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Polyester water dispersion B-3: 11.04 parts by mass
(Vylonal (registered trademark) MD1500, manufactured by TOYOB0 CO., LTD., Tg = 77°C, solid content concentration: 30% by mass)

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

Silica particle G-1: 0.59 parts by mass
(Average particle size: 200 nm, solid content concentration: 40% by mass)

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

[0164]

(Comparative Example 1)

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 22.

(Easy-to-slip coating solution 22)

Water: 48.33 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Polyester water dispersion B-1: 15.78 parts by mass

(Solid content concentration: 30% by mass)

Silica particle G-1: 0.59 parts by mass

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

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

[0165]

(Comparative 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 23.

(Easy-to-slip coating solution 23)

Water: 45.18 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Polyester water dispersion B-2: 18.93 parts by mass

(Solid content concentration: 25% by mass)

Silica particle G-1: 0.59 parts by mass

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

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

[0166]

(Comparative 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 24.

(Easy-to-slip coating solution 24)

Water: 51.32 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Polyurethane resin water dispersion C-1: 12.79 parts by mass

(Solid content concentration: 37% by mass)

Silica particle G-1: 0.59 parts by mass

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

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

[0167]

(Comparative 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 25.

(Easy-to-slip coating solution 25)

Water: 47.39 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Polyester water dispersion B-1 (Solid content concentration: 30% by mass): 11.04 parts by mass

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

Silica particle G-1: 0.59 parts by mass
(Average particle size: 200 nm, solid content concentration: 40% by mass)

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

[0168]

(Comparative 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 26.

(Easy-to-slip coating solution 26)

Water: 49.51 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Polyester water dispersion B-1: 11.04 parts by mass

(Solid content concentration: 30% by mass)

Carbodiimide-based cross-linking agent E-1: 3.55
parts by mass

(Solid concentration: 40% by mass)

Silica particle G-1: 0.59 parts by mass
(Average particle size: 200 nm, solid content
concentration: 40% by mass)

Surfactant (fluorine-based, solid content
concentration: 10% by mass): 0.30 parts by mass
[0169]

(Comparative 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
27.

(Easy-to-slip coating solution 27)

Water: 40.44 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Acrylic polyol resin A-1: 23.67 parts by mass

(Solid content concentration: 20% by mass)

Silica particle G-1: 0.59 parts by mass
(Average particle size: 200 nm, solid content
concentration: 40% by mass)

Surfactant H-1 (fluorine-based, solid content

concentration: 10% by mass): 0.30 parts by mass

[0170]

(Comparative 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 28.

(Easy-to-slip coating solution 28)

Water: 45.65 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Acrylic polyol resin A-1: 16.57 parts by mass

(Solid content concentration: 20% by mass)

Isocyanate cross-linking agent F-1 (solid content concentration: 75% by mass): 1.89 parts by mass

Silica particle G-1: 0.59 parts by mass

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

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

[0171]

(Comparative 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 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 .

[0172]

(Comparative Example 9)

A release film for producing a super-thin layer 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).

[0173]

Table 2 shows the evaluation results of Examples and Comparative Examples.

[0174]

[Table 2]

	PET substrate	Easy-to-slip coating solution (composition ratio is represented by parts by mass of solid content)										Easy-to-slip coating layer				Physical properties of single film of easy-to-slip coating layer		Release coating solution	After release processing		Ceramic green sheet
		Easy-to-slip coating solution	Resin	Cross- linking agent	Resin/ cross- linking agent ratio (parts by mass)	Particle 1	Particle 1 ratio (parts by mass)	Particle 2	Particle 2 ratio (parts by mass)	Surfactant	Surfactant ratio (parts by mass)	Sa (μm)	P (μm)	Particle dispersibility	Rsm (μm)	Martens hardness HM (N/mm ²)	Ratio of elastic to total work nit (%)		Unwinding electric charge (kV)	Pinholes, thickness variation	
Example 1	Single layer, no lubricant	1	A-1	D-1	70/30	G-1	5	-	-	H-1	0.67	0.004	0.126	Good	2.2	235.4	37.3	X-1	0.8	Good	Good
Example 2	Single layer, no lubricant	2	A-1	E-1	70/30	G-1	5	-	-	H-1	0.67	0.004	0.197	Good	2.4	200.4	34.7	X-1	0.8	Good	Good
Example 3	Single layer, no lubricant	3	A-1	D-2	70/30	G-1	5	-	-	H-1	0.67	0.004	0.290	Good average	2.6	270.9	43.2	X-1	0.4	Good	Good
Example 4	Single layer, no lubricant	4	A-1	D-1	40/60	G-1	5	-	-	H-1	0.67	0.004	0.130	Good	2.3	233.5	38.2	X-1	0.8	Good	Good
Example 5	Single layer, no lubricant	5	A-1	D-1	85/15	G-1	5	-	-	H-1	0.67	0.004	0.135	Good	2.3	200.1	32.3	X-1	1.6	Good	Good
Example 6	Single layer, no lubricant	6	A-2	D-1	70/30	G-1	5	-	-	H-1	0.67	0.004	0.131	Good	2.3	254.3	39.1	X-1	0.8	Good	Good
Example 7	Single layer, no lubricant	7	A-3	D-1	70/30	G-1	5	-	-	H-1	0.67	0.004	0.130	Good	2.2	237.6	38.1	X-1	1.2	Good	Good
Example 8	Single layer, no lubricant	8	A-4	D-1	70/30	G-1	5	-	-	H-1	0.67	0.004	0.191	Good	2.2	200.1	32.1	X-1	3.3	Good average	Good
Example 9	Single layer, no lubricant	9	A-5	D-1	70/30	G-1	5	-	-	H-1	0.67	0.004	0.097	Good	2.3	165.4	29.1	X-1	6.2	Average	Good
Example 10	Single layer, no lubricant	10	A-6	D-1	70/30	G-1	5	-	-	H-1	0.67	0.012	0.389	Average	3.3	239.1	39.1	X-1	0.8	Good	Average
Example 11	Single layer, no lubricant	11	A-7	D-1	70/30	G-1	5	-	-	H-1	0.67	0.010	0.245	Good average	2.9	238.9	38.9	X-1	0.8	Good	Good
Example 12	Single layer, no lubricant	12	A-8	D-1	70/30	G-1	5	-	-	H-1	0.67	0.004	0.126	Good	2.2	235.1	37.5	X-1	0.8	Good	Good
Example 13	Single layer, no lubricant	13	A-9	D-1	70/30	G-1	5	-	-	H-1	0.67	0.004	0.118	Good	2.2	171.0	32.1	X-1	4.0	Good average	Good
Example 14	Single layer, no lubricant	14	A-10	D-1	70/30	G-1	5	-	-	H-1	0.67	0.004	0.123	Good	2.2	208.8	34.5	X-1	0.8	Good	Good
Example 15	Single layer, no lubricant	15	A-11	D-1	70/30	G-1	5	-	-	H-1	0.67	0.004	0.120	Good	2.2	153.2	28.2	X-1	5.1	Average	Good
Example 16	Single layer, no lubricant	16	A-12	D-1	70/30	G-1	5	-	-	H-1	0.67	0.004	0.129	Good	2.2	221.4	35.1	X-1	1.3	Good	Good
Example 17	Single layer, no lubricant	17	A-10	D-1	70/30	G-1	5	G-4	1	H-1	0.67	0.004	0.196	Good	2.3	208.8	34.5	X-1	0.5	Good	Good
Example 18	Single layer, no lubricant	18	A-10	D-1	70/30	G-2	10	G-4	1	H-1	0.67	0.004	0.198	Good	2.3	208.8	34.5	X-1	1.2	Good	Good
Example 19	Single layer, no lubricant	19	A-10	D-1	70/30	G-3	10	-	-	H-1	0.67	0.004	0.080	Good	2.1	208.8	34.5	X-1	1.8	Good	Good
Example 20	Single layer, no lubricant	20	A-10	D-1	70/30	G-5	5	-	-	H-1	0.67	0.004	0.102	Good	2.1	208.8	34.5	X-1	1.0	Good	Good
Example 21	Single layer, no lubricant	1	A-1	D-1	70/30	G-1	5	-	-	H-1	0.67	0.004	0.126	Good	2.2	235.4	37.3	X-2	0.4	Good	Good

Example 22	Single layer, no lubricant	21	B-3	D-1	70/30	G-1	5	-	-	H-1	0.67	0.004	0.134	Good	2.2	268.2	28.7	X-1	5.6	Average	Good
Comparative Example 1	Single layer, no lubricant	22	B-1	-	100/0	G-1	5	-	-	H-1	0.67	0.005	0.092	Good	2.2	262.6	26.7	X-1	12.6	Poor	Good
Comparative Example 2	Single layer, no lubricant	23	B-2	-	100/0	G-1	5	-	-	H-1	0.67	0.003	0.105	Good	2.2	251.6	24.4	X-1	14.6	Poor	Good
Comparative Example 3	Single layer, no lubricant	24	C-1	-	100/0	G-1	5	-	-	H-1	0.67	0.004	0.110	Good	2.2	87.6	37.1	X-1	17.4	Poor	Good
Comparative Example 4	Single layer, no lubricant	25	B-1	D-1	70/30	G-1	5	-	-	H-1	0.67	0.009	0.407	Average	2.9	240.0	26.3	X-1	11.6	Poor	Average
Comparative Example 5	Single layer, no lubricant	26	B-1	E-1	70/30	G-1	5	-	-	H-1	0.67	0.007	0.119	Good	2.2	232.1	24.3	X-1	11.8	Poor	Good
Comparative Example 6	Single layer, no lubricant	27	A-1	-	100/0	G-1	5	-	-	H-1	0.67	0.004	0.110	Good	2.2	124.3	28.4	X-1	10.6	Poor	Good
Comparative Example 7	Single layer, no lubricant	28	A-1	F-1	70/30	G-1	5	-	-	H-1	0.67	0.004	0.352	Average	2.8	145.4	28.9	X-1	10.1	Poor	Average
Comparative Example 8 ^{*1}	E5000	-										(0.031)	(0.769)	-	(30.2)	-	-	X-1	0.4	Good	Poor
Comparative Example 9 ^{*1}	Laminated film Z	-										(0.028)	(0.754)	-	(30.0)	-	-	X-1	0.4	Good	Poor

*1: In the "easy-to-slip coating layer" columns of Comparative Examples 8 and 9, the evaluation results of the surface opposite to the laminated surface of the "release coating layer" of the polyester film are described.

[0175]

In Table 2 above, for the resin, the cross-linking agent, the particles, and the surfactant in the easy-to-slip coating solution, respective compositions are described as parts by mass of the solid content. The sum of parts by mass of the solid contents of the resin, the cross-linking agent, the particles, and the surfactant present in the easy-to-slip coating solution is the parts by mass of the total solid content of the easy-to-slip coating layer. By dividing the parts by mass of the solid content of each of the resin, the cross-linking agent, the particles, and the surfactant by the parts by mass of the total solid content of the easy-to-slip coating layer, the mass percentages of the resin, the cross-linking agent, the particles, and the surfactant in the total solid content of the easy-to-slip coating layer can be obtained.

[0176]

In Examples 1 to 22, the unwinding electric charge was low when the roll was unwound after release processing again, to cause the environmental foreign matters to be less likely to adhere, whereby a high-quality ceramic capacitor could be prepared without reducing the yield of the ceramic capacitor. The release film includes: 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 other surface of the substrate. A single film of a mixture composition comprising a resin and a cross-linking agent both used in the easy-to-slip coating layer has a Martens hardness (HM) of 150 N/mm² or more. This provides an increased crosslinking density of the easy-to-slip coating layer and a decreased deformation amount of the easy-to-slip coating layer when being wound up after release processing. The single film has a ratio of elastic to total work (η_{it}) of 28% or more, whereby the deformation of the easy-to-slip coating layer is immediately recovered due to a decrease in pressure during unwinding of the film roll. This is considered to provide a reduced contact area between the easy-to-slip coating layer and the release coating layer during unwinding the film roll, whereby the electric charge amount can be suppressed.

Meanwhile, Comparative Examples 1 to 7 do not satisfy the ranges of the Martens hardness (HM) and ratio of elastic to total work (η_{it}) of a single film of a mixture composition comprising a resin and a cross-linking agent both used in the easy-to-slip coating layer specified in the present invention. Therefore, it is considered that the contact area increases when the film roll that has been subjected to release processing is unwound to peel off the

release layer and the easy-to-slip layer, so that the unwinding electric charge increases. In Comparative Examples 8 and 9, the unwinding electric charge is low, but Comparative Examples 8 and 9 do not have the easy-to-slip coating layer specified in the present invention, and the surface roughness of the easy-to-slip coating surface increases, so that pinholes occur in the ceramic sheet.

INDUSTRIAL APPLICABILITY

[0177]

The present invention can provide a release film for producing a ceramic green sheet, which can achieve both prevention of pinholes and partial thickness variation and the like and prevention of adhesion of environmental foreign matters due to electric charge even when the ceramic green sheet is reduced in thickness. The use of the release film for producing 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:

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

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

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

wherein:

the easy-to-slip coating layer is obtained by curing a composition containing a binder resin and at least one cross-linking agent selected from an oxazoline-based cross-linking agent or a carbodiimide-based cross-linking agent;

15 the easy-to-slip coating layer has an 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 (RSm) of a roughness curve element of 10 μm or less; and

20 a single film of a mixture composition comprising a resin and a cross-linking agent both used in the easy-to-slip coating layer has a Martens hardness (HM) of 150 N/mm^2 or more and a ratio of elastic to total work (η_{it}) of 28% or more.

2. The release film for producing a ceramic green sheet according to claim 1, wherein the binder resin contains an acrylic resin.

30

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.

5

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.

10

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 or more and 2.0 μm or less.

15

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.