

DESCRIPTION

Title of Invention

MOLD RELEASE FILM

Technical Field

[0001]

The present invention relates to a release film having an antistatic layer, and in particular, to a casting film that is used for a production process of a multi-layered ceramic capacitor.

Background Art

[0002]

In recent years, in multi-layered ceramic capacitors, downsizing and weight reduction are advanced. Because of this, a demand of thinning of a ceramic green sheet is increasing year by year, too, and green sheets of less than 1 μm have been produced. In such thin ceramic green sheets, a pin hole is liable to be produced, and the presence of even a slight irregularity results in a defective product, so that there is a tendency that the yield decreases. Usually, it is general that the ceramic green sheet is produced by coating a ceramic slurry on a release film. In order to prevent the formulation of the aforementioned pin hole or irregularity, a release film with high surface smoothness has been required.

Meanwhile, with respect to a release film with high surface smoothness, on the occasion of winding up in a roll shape, blocking occurs, so that inconvenience, such as the generation of electrification at the time of roll unwinding, etc., is liable to occur. In order to prevent such inconvenience from occurring, it is known to incorporate an antistatic agent or the like in a release film, thereby imparting an antistatic function thereto.

[0003]

Recently, there is a case where a conductive polymer, such as PEDOT-PSS (a mixture of polyethylene dioxythiophene and polystyrene sulfonate), etc., is used as the antistatic agent that is used for the release film. For example, as disclosed in PTL 1, there is a case where a release layer of the release film is formed of a release agent composition composed of a curable silicone emulsion, a curing agent, and PEDOT-PSS.

In addition, there is a case where an antistatic layer is provided in the release film separately from the release layer. It is known that the antistatic layer is formed of, for example, a resin composition in which a conductive polymer, such as PEDOT-PSS, etc., is mixed in a polyester resin, a urethane resin, an acrylic resin, or the like (see PTL 2), or a resin composition in which a conductive polymer, such as PEDOT-PSS, etc., is mixed in a photocurable coating agent (see PTL 3).

Citation List

Patent Literature

[0004]

PTL 1: JP 2003-251756 A

PTL 2: JP 2012-224011 A

PTL 3: JP 2010-6079 A

Summary of Invention

Technical Problem

[0005]

However, when PEDOT-PSS is blended in the release agent composition as in PTL 1, compatibility between the silicone emulsion that is a release agent component and PEDOT-PSS is poor, so that PEDOT-PSS causes cohesion to likely form a coarse projection. For that reason, it becomes difficult to make the surface of the release film smooth. In addition, even in the resin composition described in PTL 3, PEDOT-PSS is liable to cause cohesion, so that it becomes difficult to secure the surface smoothness of the antistatic layer and the release layer formed on the antistatic layer.

Meanwhile, since the resin composition described in PTL 2 is of a non-crosslinking type, the coating strength or the like does not become sufficient, so that inconvenience, such as deterioration in solvent resistance of the antistatic layer and overcoating properties of the antistatic layer, namely coating properties of a coating solution of a release layer or the like which is to be formed on the antistatic layer, is liable to occur.

[0006]

In view of the foregoing problems, the present invention has been made, and a problem thereof is to provide a release film that is excellent in antistatic performance, solvent resistance, and overcoating properties while making its

surface smooth.

Solution to Problem

[0007]

As a result of extensive and intensive investigations made by the present inventors, it has been found that the aforementioned problem can be solved by forming an antistatic layer having a predetermined thickness on a smooth substrate surface by using an aqueous and thermosetting resin composition containing a polythiophene-based conductive polymer, such as PEDOT-PSS, thereby leading to accomplishment of the present invention. Specifically, the present invention provides the following (1) to (9).

(1) A release film including a substrate, an antistatic layer provided on one surface of the substrate, and a release layer provided on the antistatic layer or on the side of the other surface of the substrate,

the one surface of the substrate having an arithmetic average roughness Ra of 15 nm or less and a maximum projection height Rp of 150 nm or less,

the antistatic layer being formed by curing an aqueous thermosetting resin composition containing a polythiophene-based conductive polymer (A), and

the antistatic layer having a thickness of 12 to 250 nm.

(2) The release film as set forth in the above (1), wherein the release layer is provided on the antistatic layer.

(3) The release film as set forth in the above (1) or (2), wherein the release layer has an arithmetic average roughness Ra of less than 10 nm and a maximum projection height Rp of less than 100 nm.

(4) The release film as set forth in any of the above (1) to (3), wherein the aqueous thermosetting resin composition further contains a hydroxy group-containing polyester resin (B) and a melamine compound (C).

(5) The release film as set forth in the above (4), wherein the aqueous thermosetting resin composition contains the melamine compound (C) in an amount of 8 to 35 parts by mass based on 100 parts by mass of a sum total of the polythiophene-based conductive polymer (A) and the hydroxy group-containing polyester resin (B).

(6) The release film as set forth in the above (4) or (5), wherein the aqueous thermosetting resin composition contains the polythiophene-based conductive polymer (A) in an amount of 0.5 to 50 parts by mass based on 100 parts by mass of

the hydroxy group-containing polyester resin (B).

(7) The release film as set forth in any of the above (4) to (6), wherein the melamine compound (C) is a methylol melamine.

(8) The release film as set forth in any of the above (1) to (7), wherein the polythiophene-based conductive polymer (A) is a mixture of polyethylene dioxythiophene and polystyrene sulfonate (PEDOT-PSS).

(9) The release film as set forth in any of the above (1) to (8), which is to be used for a production process of a ceramic green sheet.

Advantageous Effects of Invention

[0008]

The present invention is able to provide a release film that is excellent in antistatic performance, solvent resistance, and overcoating properties while making its surface smooth.

Brief Description of Drawings

[0009]

Fig. 1 is a schematic cross-sectional view showing an embodiment of the release film of the present invention.

Fig. 2 is a schematic cross-sectional view showing another embodiment of the release film of the present invention.

Description of Embodiments

[0010]

The present invention is hereunder described in more detail by reference to embodiments.

The release film of the present invention includes a substrate, an antistatic layer provided on one surface of the substrate, and a release layer provided on the antistatic layer or on the side of the other surface of the substrate.

More specifically, as the release film, a release film 10A as shown in Fig. 1, including a substrate 11, an antistatic layer 12 provided on one surface 11A of the substrate 11, and a release layer 13 provided on this antistatic layer 12, is exemplified. The release film may also be a release film 10B as shown in Fig. 2, in which the antistatic layer 12 is provided on the one surface 11A of the substrate 11, and the release layer 13 is provided on the other surface 11B of the substrate 11.

[0011]

The release film wound up in a roll shape causes blocking according to circumstances, and on the occasion of unwinding the release film from the roll, static electricity is produced. In view of the fact that the release film has the antistatic layer, it prevents such unwinding electrification, thereby preventing blocking or worsening of wind-up properties. In addition, on the occasion of releasing an article of every sort as laminated on the release layer, such as a ceramic green sheet, etc., from the release film, release failure due to the electrification is hardly caused. Furthermore, attachment of dust or the like onto the release layer due to static electricity is prevented from occurring, too.

The release film is preferably one as shown in Fig. 1, in which the release layer 13 is provided on the antistatic layer 12. In such a release film, the electrification on the release layer 13 is more easily prevented by the antistatic layer 12 from occurring.

[0012]

Next, each of the members of the release film is described in detail.

[Substrate]

The substrate is one in which one surface of the substrate on which the antistatic layer is formed (surface 11A in Figs. 1 and 2) has an arithmetic average roughness Ra of 15 nm or less and a maximum projection height Rp of 150 nm or less. In the present invention, when the arithmetic average roughness Ra or maximum projection height Rp of the one surface of the substrate is more than the foregoing upper value, even if the composition for forming the antistatic layer is an aqueous thermosetting resin composition as mentioned later, the surface of the antistatic layer is hardly made smooth. When the surface of the antistatic layer cannot be made smooth, for example, in the case of providing a thin layer, such as a release layer, etc., on the antistatic layer, the surface of such a release layer or the like cannot be made smooth, and an irregularity or a pin hole is liable to be produced on an article to be laminated on the release layer, such as a ceramic green sheet, etc.

From the foregoing viewpoints, the aforementioned arithmetic average roughness Ra and maximum projection height Rp are preferably 12 nm or less and 120 nm or less, respectively. In addition, taking into consideration easiness of production of the substrate, and so on, the arithmetic average roughness Ra and the maximum projection height Rp are preferably 1 nm or more and 5 nm or more,

respectively.

[0013]

The substrate is not particularly limited so long as the arithmetic average roughness R_a and the maximum projection height R_p fall within the aforementioned ranges, respectively. Examples thereof include films made of a plastic such as a polyester, e.g., polyethylene terephthalate, polyethylene naphthalate; a polyolefin, e.g., polypropylene, polymethylpentene; polycarbonate; and polyvinyl acetate. These may be a single layer, or may be a multilayer of two or more layers of the same kind or a different kind. Among them, a polyester film is preferred, and a polyethylene terephthalate film is especially preferred. In the polyethylene terephthalate film, since dust or the like is hardly generated at the time of processing, use, or the like, for example, ceramic slurry coating failure, etc. due to dust or the like can be effectively prevented from occurring.

In addition, a thickness of the substrate is not particularly limited, and it is typically approximately 10 to 300 μm , and preferably approximately 15 to 200 μm .

In order to secure the aforementioned arithmetic average roughness R_a and maximum projection height R_p , it is suitable that the substrate does not contain particles; however, the substrate may contain particles so long as the aforementioned arithmetic average roughness R_a and maximum projection height R_p can be secured. In the case where the substrate contains particles, in order to make the arithmetic average roughness R_a and the maximum projection height R_p of the substrate small, the particle diameter of the particles (for example, a filler for imparting sliding property, such as silica, calcium carbonate, titanium oxide, etc.) may be made small, or the blending amount of the particles may be reduced.

[0014]

[Antistatic Layer]

The antistatic layer is one obtained by curing an aqueous thermosetting resin composition containing a polythiophene-based conductive polymer (A) (hereinafter also referred to simply as "component (A)").

In the present invention, when the resin composition that forms the antistatic layer is made thermosetting, the coating strength of the antistatic layer is improved, and therefore, the solvent resistance of the antistatic layer becomes favorable. Furthermore, in the case of providing a thin layer, such as a release

layer, etc., on the antistatic layer, overcoating properties of the thin layer become favorable. That is, on the occasion of forming a thin layer, such as a release layer, etc., on the antistatic layer, the generation of uneven coating or the generation of cissing, stripes, etc. is prevented from occurring.

In addition, by making the composition aqueous, the polythiophene-based conductive polymer (A) is easily dispersed or dissolved in the composition without causing cohesion or the like, so that the antistatic layer or the release layer to be formed thereon, or the like can be made smooth. Furthermore, the production of an irregularity or a pin hole on the release layer, etc. which is formed on the antistatic layer is prevented from occurring.

[0015]

In addition, a thickness of the antistatic layer is 12 to 250 nm. When the thickness of the antistatic layer is less than 12 nm, the thickness is too thin, so that a surface resistance value of the antistatic layer is not sufficiently reduced due to the component (A), and the antistatic performance is hardly imparted. In addition, a sufficient film cannot be formed, and the solvent resistance or overcoating properties become low. On the other hand, where the thickness of the antistatic layer is more than 250 nm, even when the one surface of the substrate is made as a smooth surface, the surface of the antistatic layer is hardly made smooth, and it becomes difficult to secure the surface smoothness of the release layer, etc. which is formed on the antistatic layer. From the foregoing viewpoints, the thickness of the antistatic layer is preferably 15 to 200 nm. The thickness of the antistatic layer is one as measured with a spectroscopic ellipsometer.

In the antistatic layer, by properly changing a solid content concentration in the aqueous thermosetting resin composition or changing a gap, etc. of the coating apparatus, it becomes possible to make the antistatic layer in a desired thickness. Though the solid content concentration in the aqueous thermosetting resin composition is not particularly limited, it is preferably approximately 0.4 to 2.0% by mass, and more preferably approximately 0.5 to 1.6% by mass.

[0016]

It is preferred that the antistatic layer is composed of a cured film formed through crosslinking of a polyester resin and a melamine compound, and specifically, the antistatic layer is preferably a film obtained by curing an aqueous thermosetting resin composition containing, in addition to the aforementioned component (A), a hydroxy group-containing polyester resin (B) (hereinafter also

referred to simply as "polyester resin (B)" or "component (B)") and a melamine compound (C) (hereinafter also referred to simply as "component (C)").

The aqueous thermosetting resin composition may be a water-dispersible or water-soluble resin composition in which the respective components are dispersed or dissolved in a diluent liquid including water.

[0017]

Each of the components constituting the antistatic layer is hereunder described in more detail.

<Polythiophene-based Conductive Polymer (A)>

Examples of a specific compound of the polythiophene-based conductive polymer (A) include a mixture of a polyalkylene dioxythiophene, such as polyethylene dioxythiophene, polypropylene dioxythiophene, poly(ethylene/propylene) dioxythiophene, etc., and polystyrene sulfonate; a polythiophene-based compound having a sulfonic acid group, such as poly(3-thiophene- β -ethanesulfonic acid), etc.; and the like. Among them, a mixture of a polyalkylene dioxythiophene and polystyrene sulfonate is preferred. Above all, a mixture of polyethylene dioxythiophene and polystyrene sulfonate (PEDOT-PSS) is more preferred.

In view of the fact that the antistatic layer contains the polythiophene-based conductive polymer (A), even when the antistatic layer is a thin film, the surface resistance value is sufficiently low, so that it becomes possible to effectively prevent the electrification from occurring. In addition, the polythiophene-based conductive polymer (A) has water solubility or water dispersibility, and therefore, as described above, it becomes possible to easily achieve dissolution or dispersion in the aqueous thermosetting resin composition.

[0018]

It is preferred that the aqueous thermosetting resin composition for forming the antistatic layer contains the polythiophene-based conductive polymer (A) in an amount of 0.5 to 50 parts by mass based on 100 parts by mass of the polyester resin (B). By containing the component (A) in an amount of the aforementioned lower limit or more, it becomes possible to allow the release film to exhibit an appropriate antistatic performance. In addition, by containing the component (A) in an amount of the aforementioned upper limit or less, the cohesion of the component (A) and the generation of curing failure of the antistatic layer are prevented from occurring.

From the foregoing viewpoints, in the aqueous thermosetting resin composition, it is more preferred that the component (A) is contained in an amount of 0.6 to 20 parts by mass based on 100 parts by mass of the component (B).

[0019]

<Polyester Resin (B)>

The polyester resin (B) can be obtained by allowing a polyvalent carboxylic acid component to react with a polyhydric alcohol component. The polyester resin (B) is one containing a hydroxy group in a molecule thereof, and it is preferred that an equivalent ratio of an OH group of the alcohol component to a COOH group of the polyvalent carboxylic acid for constituting the polyester ((OH group)/(COOH group)) is more than 1.0. Since the polyester resin (B) contains a hydroxy group, it is possible for the polyester resin (B) to crosslink with the melamine compound (C).

[0020]

Here, the polyvalent carboxylic acid component is a compound having two or more carboxy groups in one molecule, and for example, polybasic acids which can be generally used for production of a polyester resin, such as phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, tetrahydroisophthalic acid, tetrahydroterephthalic acid, hexahydrophthalic acid, hexahydroisophthalic acid, hexahydroterephthalic acid, trimellitic acid, adipic acid, sebacic acid, succinic acid, azelaic acid, naphthalenedicarboxylic acid, 4,4-diphenyldicarboxylic acid, HET acid, fumaric acid, maleic acid, itaconic acid, pyromellitic acid, etc., can be used. In addition, as the polyvalent carboxylic acid component, anhydrides of the aforementioned polyvalent carboxylic acid components can also be used. These polyvalent carboxylic acid components can be used alone or in combination of two or more thereof.

[0021]

The polyhydric alcohol component is a compound having two or more hydroxy groups in one molecule, and specific examples thereof include those which are used on the occasion of producing a usual polyester resin, for example, diols, such as, ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, polyethylene glycol, polypropylene glycol, neopentylene glycol, hexylene glycol, 1,3-butylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2-butyl-2-ethyl-1,3-propanediol, methylpropanediol, cyclohexanedimethanol, 3,3-diethyl-1,5-pentanediol, etc.; trihydric or higher polyhydric alcohols, such as glycerin, trimethylolethane,

trimethylolpropane, erythritol, pentaerythritol, dipentaerythritol, etc.; and the like. These polyhydric alcohol components can be used alone or in combination of two or more thereof.

[0022]

In order that the polyester resin (B) may be used as a component of the aqueous thermosetting resin composition, a polyester resin having water solubility or water dispersibility is preferred. Though the polyester resin (B) is not particularly limited, in order to impart water solubility or water dispersibility, those including, as a constituent unit of the polyester, a constituent unit including a sulfonic acid base or a carboxylic acid base are suitably used.

The polyester resin (B) serves as a main component in the aqueous thermosetting resin composition and is contained in an amount of typically 50% by mass or more, and preferably 65 to 92% by mass relative to the total amount of solid contents in the composition. In the present specification, the total amount of solid contents refers to an amount resulting from elimination of the volatile component, such as the solvent, etc., which is volatilized during the production process, such as a curing step, etc., from the aqueous thermosetting resin composition.

[0023]

<Melamine Compound (C)>

In addition, specific examples of the melamine compound (C) include a methylol melamine and an alkoxyated methylol melamine. Of these, a methylol melamine is more preferred from the standpoints that the water solubility is high; and that a thermosetting rate is fast. Examples of the methylol melamine include those in which 1 to 6 methylol groups are bonded to the nitrogen atom(s) of the amino group(s) of melamine. In addition, examples of the alkoxyated methylol melamine include those in which at least a part of the methylol groups of the methylol melamine is alkoxyated with a lower alcohol, and specifically, examples thereof include those in which the carbon number of the alkoxy group of methoxyated methylol melamine, butoxyated methylol melamine, or the like is 1 to 4.

In addition, the melamine compound (C) is preferably a water-soluble melamine, and aqueous solutions of the aforementioned compounds are used.

In the antistatic layer, in view of the fact that the component (C) is contained in addition to the component (B), the polyester resin and the melamine

compound are crosslinked with each other, and therefore, the aforementioned overcoating properties and solvent resistance and so on become favorable.

[0024]

It is preferred that the aqueous thermosetting resin composition contains the melamine compound (C) in an amount of 8 to 35 parts by mass based on 100 parts by mass of a sum total of the component (A) and the component (B). In the antistatic layer, when the component (C) is blended in an amount of 8 parts by mass or more, the aforementioned solvent resistance and overcoating properties become favorable, and furthermore, the surface of the antistatic layer is easily made smooth. In addition, when the blending amount of the component (C) is 35 parts by mass or less, the dispersion stability of the composition becomes favorable, and a cohesion product is hardly produced.

In addition, the content of the aforementioned melamine compound (C) is more preferably 10 to 32 parts by mass based on 100 parts by mass of a sum total of the component (A) and the component (B).

[0025]

In addition, the surface resistance value of the antistatic layer is preferably less than $1 \times 10^{11} \Omega/\text{square}$, and more preferably less than $1 \times 10^{10} \Omega/\text{square}$. In view of the fact that the surface resistance value of the antistatic layer is less than $1 \times 10^{11} \Omega/\text{square}$, it becomes possible to appropriately prevent electrification of the release film from occurring. In particular, it becomes easy to suppress various failures generated on the occasion of producing a ceramic green sheet by using the release film.

[0026]

The aqueous thermosetting resin composition for forming the antistatic layer contains at least water as a diluent solvent and may further contain, as the diluent solvent, a polar solvent other than water, such as dimethyl sulfoxide, isopropyl alcohol (IPA), ethanol, etc. As the diluent solvent, it is more preferred to use one in which the water is contained in an amount of 30% by mass or more and 70% by mass or less in the whole of the solvent. When the amount of water is 70% by mass or less, cissing or the like, which may be generated on the occasion of coating the aqueous thermosetting resin composition, is hardly generated.

In addition, when the amount of water is 30% by mass or more, it becomes possible to disperse or dissolve the component (A) in the diluent liquid, and it becomes easy to prevent cohesion of the component (A) from occurring.

Furthermore, it becomes possible to easily disperse or dissolve the water-soluble or water-dispersible component (B) and the water-soluble component (C) in the composition. For that reason, it becomes possible to make coating properties of the thermosetting resin composition favorable to form an appropriate film.

[0027]

The antistatic layer is obtained by coating the aqueous thermosetting resin composition obtained by diluting at least the components (A) to (C) with the diluent solvent on the substrate and then heating and drying to achieve heat curing.

Here, a coating method of the aqueous thermosetting resin composition is not particularly limited, and examples thereof include a gravure coating method, a bar coating method, a spray coating method, a spin coating method, a knife coating method, a roll coating method, a die coating method, and the like.

The aqueous thermosetting resin composition may contain, in addition to the components (A) to (C) and the diluent solvent, a resin component other than the components (A) to (C), various additives, and so on so long as the effects of the present invention are not impaired. However, in order to secure the smoothness of the surface of the antistatic layer, it is suitable that the aqueous thermosetting resin composition does not contain a filler, such as an inorganic filler, etc.

[0028]

[Release layer]

The release layer is one constituted of a release agent. Specifically, a silicone resin-based release agent, an alkyd resin-based release agent, an olefin resin-based release agent, an acrylic resin-based release agent, a rubber-based release agent, a melamine resin-based release agent, a fluorine resin-based release agent, and so on can be used. Among them, a silicone resin-based release agent is preferred. The case of using a silicone resin-based release agent as the release agent is hereunder described in detail.

[0029]

As the silicone resin-based release agent, an addition reaction type silicone resin composition is preferably used. The addition reaction type silicone resin composition is one prepared by adding a catalyst and optionally, other additives, such as an addition reaction inhibitor, a release adjustor, an adhesion improver, a photosensitizer, etc., to a main agent composed of an addition reaction type silicone resin and a crosslinking agent.

The addition reaction type silicone resin is not particularly limited, and various materials can be used. For example, a polyorganosiloxane having an alkenyl group as a functional group in a molecule thereof can be used, and more specifically, a polydimethylsiloxane having, as the functional group, a vinyl group, a hexenyl group, or the like is exemplified.

In addition, a mixture of a linear polyorganosiloxane having an alkenyl group and having a mass average molecular weight (Mw) of, for example, 70,000 or more and a branched organosiloxane oligomer having an alkenyl group and having a mass average molecular weight (Mw) of approximately 500 to 50,000, and so on can also be used as the addition reaction type silicone resin. In the present specification, the mass average molecular weight (Mw) refers to a value as expressed in terms of polystyrene by means of gel permeation chromatography (GPC).

[0030]

Examples of the crosslinking agent include a polyorganosiloxane having hydrogen atoms bounded to at least two silicon atoms in one molecule, and specifically, polymethylhydrogen siloxane is exemplified. The use amount of the crosslinking agent is selected within a range of preferably 0.1 to 100 parts by mass, and more preferably 0.5 to 25 parts by mass based on 100 parts by mass of the addition reaction type silicone resin. In addition, a platinum-based catalyst is used as the catalyst.

[0031]

In order that an irregularity or a pin hole may not be produced on an article to be laminated on the release layer, such as a ceramic green sheet, etc., it is preferred that the surface of the release layer is smooth. Specifically, it is preferred that the surface of the release layer has not only an arithmetic average roughness Ra of less than 10 nm but also a maximum projection height Rp of less than 100 nm, and it is more preferred that the surface of the release layer has not only an arithmetic average roughness Ra of 8 nm or less but also a maximum projection height Rp of 80 nm or less. In addition, taking into consideration easiness of production of the release layer, and the like, it is preferred that the arithmetic average roughness Ra and the maximum projection height Rp are 1 nm or more and 10 nm or more, respectively.

In the present invention, as described above, by not only regulating the arithmetic average roughness Ra and the maximum projection height Rp of the

substrate to the predetermined values or less, respectively but also regulating the constitution of the antistatic layer to the predetermined constitution, it becomes possible to make the arithmetic average roughness Ra and the maximum projection height Rp of the release layer to be formed on the antistatic layer small as described above.

[0032]

As the release agent that constitutes the release layer, though both a non-solvent type and an aqueous type using water as the diluent solvent can be used, it is preferred to use a solvent type using an organic solvent as the diluent solvent. By using a solvent-type release agent, various release agents can be broadly used, and it becomes easy to design a required performance of every sort, such as a release performance, etc., to a desired performance.

In the case where the release agent is of a solvent type, specific examples of the organic solvent which is used as the diluent solvent include toluene, IPA, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), and the like. Since the antistatic layer has a favorable solvent resistance as described above, even when a solvent-type release agent is used as the release agent, on the occasion of forming the release layer, failure, such as dissolution of the antistatic layer, etc., is prevented from occurring.

[0033]

It is possible to form the release layer by coating the release agent composition on the antistatic layer or on the other surface of the substrate (namely, the surface of the substrate on the side at which the antistatic layer is not provided) and thereafter, subjecting the coating film to heating and drying to achieve curing. In addition, a coating method of the release agent is not particularly limited, and examples thereof include a gravure coating method, a bar coating method, a spray coating method, a spin coating method, a knife coating method, a roll coating method, a die coating method, and the like.

Though a thickness of the release layer is not particular limited, it is preferably regulated such that the basis weight after drying is approximately 0.03 to 0.4 g/m².

[0034]

[Use Method of Release film]

The release film is preferably one which is used for a production process of a multi-layered ceramic capacitor, and more preferably one which is used for a

production process of a ceramic green sheet. Specifically, the ceramic green sheet is one produced by coating a ceramic slurry on the release layer of the release film and then properly drying, etc. In addition, the release film may also be one which is used when various materials, besides the ceramic green sheet, are coated on the release layer and properly cured, etc. to produce an article in a sheet shape, or may be used for other applications. After the sheet production, the ceramic green sheet or other article produced on the release film is released from the release film.

Examples

[0035]

The present invention is hereunder described in more detail on the basis of Examples, but it should be construed that the present invention is by no means limited by these Examples.

[0036]

The measurement methods and evaluation methods in the present invention are as follows.

[Measurement Method of Thickness of Antistatic Layer]

The measurement was performed with a spectroscopic ellipsometer "M-2000", manufactured by J.A. Woollam Japan.

[Evaluation of Surface Resistance Value]

The surface resistance value of the antistatic layer was measured according to the following method.

Measurement device:

"HIRESTA UP", manufactured by Mitsubishi Chemical Analytech Co., Ltd.

Measurement condition:

Applied voltage, 100 V; measurement time: 10 seconds, the measured value is an average value of those obtained through measurement of 5 times

[Evaluation of Coating Properties of Antistatic Layer]

The surface of the antistatic layer formed on the substrate was rubbed 10 times by a finger, and smear and rubbing-off were judged through visual inspection under a fluorescent lamp according to the following criteria.

A: Not changed.

B: Either smear or rubbing-off occurred.

[Evaluation of Solvent Resistance]

An appropriate amount of a solvent (MEK) was contained in BEMCOT (model number: AP-2), manufactured by Asahi Kasei Corporation; the surface of the antistatic layer formed on the substrate was wiped up by 20 reciprocations in a length of 10 cm under a load of about 100 g/cm² at a rate of approximately one second per reciprocation; and the presence or absence of rubbing-off was confirmed through visual inspection under a fluorescent lamp according to the following criteria.

A: Not changed.

B: Rubbing-off occurred.

[Evaluation of Overcoating Properties]

In each of the Examples and Comparative Examples, whether or not the surface on which the release agent composition was coated caused any failure (whitening, unevenness, or scratches) in the surface state due to the diluent solvent of the release agent composition, or whether or not the formed release layer caused any failure (cissing or stripes) in the surface state, was confirmed through visual inspection under a fluorescent lamp. The case where the aforementioned failure was not generated was judged as "A", whereas the case where even one failure was generated was judged as "B".

[Measurement of Surface Roughness]

The arithmetic average roughness Ra and the maximum projection height Rp were measured on the basis of JIS B0601-1994 under the following conditions. Measurement device:

Optical interference type surface roughness meter, "WYKO-1100" manufactured by Veeco Instruments Inc.

Measurement Conditions:

PSI mode, lens with a magnification of 50 times

[0037]

[Example 1]

(Formation of Antistatic Layer)

100 parts by mass of a diluent liquid A (S-495, manufactured by Chukyo Yushi Co., Ltd., solid content: 8.2% by mass) obtained by diluting 8.4 parts by mass of a water-soluble hydroxy group-containing polyester resin (component (B)) and 0.5 parts by mass of PEDOT-PSS (component (A)) with 15 parts by mass of dimethyl sulfoxide and 85 parts by mass of water was mixed with 1.7 parts by mass of a melamine compound solution (P-795, manufactured by Chukyo Yushi

Co., Ltd., solid content: 70.0% by mass) composed of 70 parts by mass of a water-soluble methylol melamine (component (C)) and 30 parts by mass of water, and a mixed solvent of water and IPA (mass ratio: 1/1) was further added thereto to dilute the mixture such that a solid content was 0.6% by mass, thereby obtaining a coating solution of a thermosetting resin composition.

This coating solution of the thermosetting resin composition was uniformly coated on a substrate made of a polyethylene terephthalate film (thickness: 31 μm ; the surface to be coated with the coating solution having an arithmetic average roughness R_a of 10 nm and a maximum projection height R_p of 80 nm) such that a film thickness after drying was 15 nm, and the resultant was dried at 120°C for 60 seconds to form an antistatic layer.

[0038]

(Formation of Release layer)

A mixture (mass average molecular weight: 287,000) of a linear polyorganosiloxane modified with trivinyl at the both terminals, a branched vinyl-modified organosiloxane oligomer, and polymethylhydrogen siloxane was diluted with MEK such that a solid content was 30% by mass. To 100 parts by mass of this diluent liquid, 2 parts by mass of a platinum-based catalyst (PL-50T, manufacture by Shin-Etsu Chemical Co., Ltd.) was added, and the mixture was regulated with MEK such that a solid content concentration was 0.7% by mass, thereby obtaining a coating solution of an addition reaction type silicone resin composition.

The obtained coating solution was uniformly coated on the antistatic layer by the bar coating method such that a film thickness after drying was 0.04 g/m² in terms of a basis weight, and then dried at 130°C for one minute to form a release layer, thereby obtaining a release film in which the release layer was laminated on the antistatic layer.

[0039]

[Example 2]

The same procedures as in Example 1 were carried out, except that the addition amount of the mixed solvent of water and IPA (mass ratio: 1/1) was regulated such that the solid content concentration of the coating solution of the thermosetting resin composition was 1.5% by mass; and that the thickness of the antistatic layer was 200 nm.

[0040]

[Example 3]

The same procedures as in Example 1 were carried out, except that the blending amount of the melamine compound solution was changed to 3.5 parts by mass based on 100 parts by mass of the diluent liquid A.

[0041]

[Example 4]

The same procedures as in Example 3 were carried out, except that the addition amount of the mixed solvent of water and IPA (mass ratio: 1/1) was regulated such that the solid content concentration of the coating solution of the thermosetting resin composition was 1.5% by mass; and that the thickness of the antistatic layer was 200 nm.

[0042]

[Example 5]

The same procedures as in Example 1 were carried out, except that the blending amount of the melamine compound solution was changed to 1.45 parts by mass based on 100 parts by mass of the diluent liquid A.

[0043]

[Example 6]

(Formation of Antistatic Layer)

100 parts by mass of a diluent liquid A (S-495, manufactured by Chukyo Yushi Co., Ltd., solid content: 8.2% by mass) obtained by diluting 8.4 parts by mass of a water-soluble hydroxy group-containing polyester resin (component (B)) and 0.5 parts by mass of PEDOT-PSS (component (A)) with 15 parts by mass of dimethyl sulfoxide and 85 parts by mass of water was mixed with 1.7 parts by mass of a melamine compound solution (P-795, manufactured by Chukyo Yushi Co., Ltd., solid content: 70.0% by mass) composed of 70 parts by mass of a water-soluble methylol melamine (component (C)) and 30 parts by mass of water, and a mixed solvent of water and IPA (mass ratio: 1/1) was further added thereto to dilute the mixture such that a solid content was 0.6% by mass, thereby obtaining a coating solution of a thermosetting resin composition.

This coating solution of the thermosetting resin composition was uniformly coated on a substrate made of a polyethylene terephthalate film (thickness: 31 μm ; the surface to be coated with the coating solution having an arithmetic average roughness Ra of 10 nm and a maximum projection height Rp of 80 nm) such that a film thickness after drying was 15 nm, and the resultant was

dried at 120°C for 60 seconds to form an antistatic layer.

[0044]

(Formation of Release layer)

A mixture (mass average molecular weight: 287,000) of a linear polyorganosiloxane modified with trivinyl at the both terminals, a branched vinyl-modified organosiloxane oligomer, and polymethylhydrogen siloxane was diluted with MEK such that a solid content was 30% by mass. To 100 parts by mass of this diluent liquid, 2 parts by mass of a platinum-based catalyst (PL-50T, manufacture by Shin-Etsu Chemical Co., Ltd.) was added, and the mixture was regulated with MEK such that a solid content concentration was 0.7% by mass, thereby obtaining a coating solution of an addition reaction type silicone resin composition.

The obtained coating solution was uniformly coated on a polyethylene terephthalate film on the opposite surface to the antistatic layer by the bar coating method such that a film thickness after drying was 0.04 g/m² in terms of a basis weight, and then dried at 130°C for one minute to form a release layer, thereby obtaining a release film in which the antistatic layer and the release layer were laminated.

[0045]

[Comparative Example 1]

An antistatic layer was formed in the same manner as in Example 1, except that the addition amount of the mixed solvent of water and IPA (mass ratio: 1/1) was regulated such that the solid content concentration of the coating solution of the thermosetting resin composition was 0.5% by mass; and that the coating solution was coated in a film thickness after drying of 10 nm. Thereafter, a release layer was formed on the antistatic layer in the same manner as in Example 1.

[0046]

[Comparative Example 2]

An antistatic layer was formed in the same manner as in Example 1, except that the addition amount of the mixed solvent of water and IPA (mass ratio: 1/1) was regulated such that the solid content concentration of the coating solution of the thermosetting resin composition was 2.0% by mass; and that the coating solution was coated in a film thickness after drying of 300 nm. Thereafter, a release layer was formed on the antistatic layer in the same manner as in Example 1.

[0047]

[Comparative Example 3]

The diluent liquid A was added and diluted with a mixed solvent of water and IPA (mass ratio: 1/1) such that a solid content was 0.6% by mass, thereby obtaining a coating solution of a resin composition. This resin composition does not contain the melamine compound (C) and does not have thermosetting properties. The coating solution of the resin composition was uniformly coated on the same substrate as in Example 1 such that a film thickness after drying was 15 nm, and the resultant was dried at 120°C for 60 seconds to form an antistatic layer. Thereafter, a release layer was formed on the antistatic layer in the same manner as in Example 1.

[0048]

[Comparative Example 4]

125 parts by mass of a binder solution containing 75 parts by mass of an acrylic monomer mixture containing dipentaerythritol hexaacrylate, dipentaerythritol triacrylate, and N-vinylpyrrolidone in a proportion of 45/20/10 in terms of a mass ratio, 20 parts by mass of butyl acetate, and 30 parts by mass of IPA was mixed with 15.5 parts by mass of an aqueous solution containing PEDOT-PSS in a proportion of 1.3% by mass and 0.2 parts by mass of α -hydroxycyclohexylphenyl methanone (photoinitiator), and the mixture was diluted with IPA such that a total amount of the acrylic monomer mixture and PEDOT-PSS was 2.5% by mass, thereby obtaining a coating solution of a photocurable resin composition.

This coating solution of the photocurable resin composition was uniformly coated on the same substrate as in Example 1 such that a film thickness after drying was 100 nm, and the resultant was dried at 70°C for 60 seconds, followed by irradiation with ultraviolet rays at a quantity of light of 200 mJ/cm² to form an antistatic layer. Thereafter, a release layer was formed on the antistatic layer in the same manner as in Example 1.

[0049]

[Comparative Example 5]

A partial hydrolysate of tetraethoxysilane (N-103X, manufactured by Colcoat Co., Ltd.) was diluted with IPA such that a solid content was 0.6% by mass, to prepare a resin coating solution. This resin coating solution was uniformly coated on the same substrate as in Example 1 such that a film thickness after

drying was 70 nm, and the resultant was dried at 120°C for 60 seconds to form an antistatic layer. Thereafter, a release layer was formed on the antistatic layer in the same manner as in Example 1.

[0050]
Table 1

	Antistatic layer				Evaluation of antistatic layer			Surface roughness of release layer (nm)	
	Component (A) parts by mass	Component (C) parts by mass	Thickness nm	Surface resistance value Ω/square	Coating properties	Solvent resistance	Overcoating properties	Ra	Rp
Example 1	6.0	14.6	15	3×10^9	A	A	A	5	60
Example 2	6.0	14.6	200	9×10^8	A	A	A	5	60
Example 3	6.0	30.0	15	4×10^9	A	A	A	5	60
Example 4	6.0	30.0	200	9×10^8	A	A	A	5	60
Example 5	6.0	12.4	15	3×10^9	A	A	A	5	60
Example 6	6.0	14.6	15	3×10^9	A	A	A	5	60
Comparative Example 1	6.0	14.6	10	3×10^{10}	A	B	B	5	60
Comparative Example 2	6.0	14.6	300	2×10^7	A	A	A	8	100
Comparative Example 3	6.0	0	15	3×10^9	A	B	B	5	60
Comparative Example 4	-	-	100	4×10^9	A	A	A	7	150
Comparative Example 5	-	-	70	4×10^9	A	B	B	8	110

*: In Table 1, the term "parts by mass" of the component (A) (PEDOT-PSS) expresses "parts by mass" based on 100 parts by mass of the component (B). The term "parts by mass" of the component (C) (melamine compound) expresses "parts by mass" based on 100 parts by mass of a sum total of the component (A) and the component (B).

[0051]

In the foregoing Examples 1 to 5, by forming the antistatic layer having a predetermined thickness on the smooth substrate by using the aqueous thermosetting resin composition containing PEDOT-PSS, the coating properties, solvent resistance, and overcoating properties of the antistatic layer were able to be made favorable while making the antistatic performance of the release film favorable. In addition, since the smoothness of the surface of the antistatic layer was able to be secured, the arithmetic average roughness Ra and the maximum projection height Rp of the release layer formed on the antistatic layer became low, so that the smoothness of the release layer was able to be secured. Furthermore, in Example 6, though the release layer was provided on the surface of the substrate at the opposite side to the surface on which the antistatic layer was provided, the various performances were able to be made favorable.

On the other hand, in the release film of Comparative Example 1, since the antistatic layer was thin, the surface resistance value was high so that the sufficient antistatic performance wasn't able to be revealed, and the solvent resistance and the overcoating properties were insufficient, too. In addition, in Comparative Example 2, since the antistatic layer was too thick, the smoothness of the surface of the antistatic layer wasn't able to be secured, and the surface roughness of the release layer also became large.

Furthermore, in Comparative Examples 3 and 4, since the resin composition did not have aqueous and thermosetting properties, the solvent resistance and the overcoating properties were insufficient, and cohesion was generated in the component (A), so that the smoothness wasn't able to be sufficiently secured. In addition, in the release film of Comparative Example 5, the antistatic layer is one not containing the component (A), and not only the solvent resistance and the overcoating properties of the antistatic layer were poor, but also the surface roughness of the release layer increased so that the smoothness wasn't able to be sufficiently secured.

Reference Signs List

[0052]

10A, 10B: Release film

11: Substrate

11A: One surface

12: Antistatic layer

13: Release layer

CLAIMS**[Claim 1]**

A release film comprising a substrate, an antistatic layer provided on one surface of the substrate, and a release layer provided on the antistatic layer or on the side of the other surface of the substrate,

the one surface of the substrate having an arithmetic average roughness Ra of 15 nm or less and a maximum projection height Rp of 150 nm or less,

the antistatic layer being formed by curing an aqueous thermosetting resin composition comprising a polythiophene-based conductive polymer (A),

the antistatic layer having a thickness of 12 to 250 nm,

wherein the aqueous thermosetting resin composition further comprises a hydroxy group-containing polyester resin (B) and a melamine compound (C), and

wherein the aqueous thermosetting resin composition comprises the melamine compound (C) in an amount of 8 to 35 parts by mass based on 100 parts by mass of a sum total of the polythiophene-based conductive polymer (A) and the hydroxy group-containing polyester resin (B).

[Claim 2]

The release film according to claim 1, wherein the release layer is provided on the antistatic layer.

[Claim 3]

The release film according to claim 1 or 2, wherein the release layer has an arithmetic average roughness Ra of less than 10 nm and a maximum projection height Rp of less than 100 nm.

[Claim 4]

The release film according to claim 1, wherein the aqueous thermosetting resin composition comprises the polythiophene-based conductive polymer (A) in an amount of 0.5 to 50 parts by mass based on 100 parts by mass of the hydroxy group-containing polyester resin (B).

[Claim 5]

The release film according to any one of claims 1 to 4, wherein the melamine compound (C) is a methylol melamine.

[Claim 6]

The release film according to any one of claims 1 to 5, wherein the polythiophene-based conductive polymer (A) is a mixture of polyethylene dioxythiophene and polystyrene sulfonate.

[Claim 7]

The release film according to any one of claims 1 to 6, which is to be used for a production process of a ceramic green sheet.