

DESCRIPTION

TITLE OF THE INVENTION: SILICONE-RELEASE-TYPE POLYESTER
FILM AND METHOD FOR MANUFACTURING SAME

TECHNICAL FIELD

[0001]

The present invention relates to a silicone-release polyester film. More specifically, the present invention relates to a silicone-release polyester film having light peelability optimum for ceramic green sheet forming to be used for manufacture of a stacked ceramic capacitor and being capable of preventing the rupture of a sheet and the occurrence of pinholes during the peeling or lamination of a ceramic green sheet, a method for manufacturing the same, an article to be protected on which the silicone-release polyester film is laminated, and the like.

BACKGROUND ART

[0002]

In the manufacture of a stacked ceramic capacitor, a release film is used as a carrier film for forming a ceramic green sheet. As a substrate of the release film, a polyester film is used particularly in terms of dimensional stability and heat resistance. In recent years, while stacked ceramic capacitors have been miniaturized and

increased in capacity, high reliability for in-vehicle use has been required, and the demand for improvement in the quality of ceramic green sheets has been increasing.

[0003]

As the ceramic green sheet is made thinner and highly infallible, the thickness of the dried sheet has been fallen in a region of several μm or less. Therefore, the carrier film is particularly required to have light peelability. As a result of the reduction in thickness, however, the rigidity of the ceramic green sheet is reduced, so that the peeling force of the conventional release film causes breakage or deformation when the green sheet is peeled off and the chip defect rate increases. Thus, light peelability is required in order to avoid these inconveniences.

[0004]

Accordingly, it is required to reduce the peeling force of a release film, and for example, a method of adjusting the peeling force by controlling the crosslinked structure of silicone has been proposed (see, for example, Patent Document 1). However, such a method of controlling the crosslinked structure of a release layer may require new design of a polymer or a crosslinking agent having a special structure, or may require stronger energy at the time of ultraviolet irradiation, electron beam irradiation,

or the like, and there is a problem that the cost increases. In addition, a release layer including a silicone resin having a crosslinked structure and a silicone resin having no crosslinked structure has been proposed (see, for example, Patent Document 2). In this method, however, since the solvent of the coating agent for forming the release layer is an organic solvent, there is a problem that an extensive organic solvent treatment facility is needed at the time of coating and drying, and the running cost of the volatilized organic solvent treatment is also increased, resulting in an increase in cost. Furthermore, there are working environment problems, and safety problems such as organic solvent explosion and fire.

[0005]

In addition, a method in which no organic solvent is used has also been proposed (see, for example, Patent Document 3), but this method has a problem that handling of the coating agent becomes complicated due to an increase in its viscosity, so that the coating agent is difficult to apply uniformly. In addition, a method using an aqueous silicone emulsion has been proposed (see, for example, Patent Document 4). However, in this method, the surfactant (or emulsifier) used is not clearly specified, and moreover, there is a problem that because of use of no

reaction inhibitor, the emulsion is poor in stability and cannot be applied uniformly. In thinning a ceramic green sheet, the surface of a release layer is required to have very high uniformity and those methods are insufficient.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0006]

Patent Document 1: JP-A-2006-7689

Patent Document 2: JP-A-2008-254207

Patent Document 3: JP-A-2003-192987

Patent Document 4: JP-A-2009-518499

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007]

In view of the above circumstances, an object of the present invention is to provide a silicone-release polyester film superior in light peelability and release layer (film) uniformity, a method for manufacturing the same, an article to be protected on which the silicone-release polyester film is laminated, and the like.

MEANS FOR SOLVING THE PROBLEMS

[0008]

The present inventors have conducted intensive studies in order to solve the above problems. As a result, the present inventors have found that the above problems can be solved by using a specific silicone, performing a method with a catalyst for performing the silicone crosslinking reaction and a crosslinking reaction inhibitor, and applying a catalyst that maximizes the crosslinking density in a release layer forming process as much as possible, and have accomplished the present invention.

[0009]

That is, the present invention provides the following silicone-release polyester films (silicone-releasable polyester films).

[0010]

[1] A silicone-release polyester film having, on at least one side of a polyester film, a coating layer (also referred to as "release layer" in the present description) formed using a coating composition for release including an aqueous dispersion of an alkenyl group-containing silicone, an aqueous dispersion of a silicone having a hydrogen atom directly bonded to a Si atom represented by Si-H group, and an aqueous dispersion containing a platinum-based catalyst,

wherein

a platinum element amount in the platinum-based

catalyst is greater than 120 ppm and less than 600 ppm based on a weight of the alkenyl group-containing silicone;

the platinum-based catalyst includes a platinum-based catalyst containing a crosslinking reaction inhibitor and a platinum-based catalyst containing no crosslinking reaction inhibitor; and

a thickness of the coating layer is 5 nm or more and 70 nm or less.

[0011]

[2] The silicone-release polyester film according to [1], wherein

a platinum element amount (P0) of the platinum-based catalyst containing no crosslinking reaction inhibitor is 50 ppm or more and less than 400 ppm based on the weight of the alkenyl group-containing silicone, and

a platinum element amount (P1) of the platinum-based catalyst containing a crosslinking reaction inhibitor is 40 ppm or more and less than 400 ppm based on the weight of the alkenyl group-containing silicone.

[0012]

[3] The silicone-release polyester film according to [1] or [2], wherein

the platinum-based catalyst contains a platinum element amount (P0) of the platinum-based catalyst containing no crosslinking reaction inhibitor and a

platinum element amount (P1) of the platinum-based catalyst containing a crosslinking reaction inhibitor, and

a ratio ($P0/(P1 + P0)$) of the platinum element amount (P0) of the platinum-based catalyst containing no crosslinking reaction inhibitor to a total platinum element weight ($P1 + P0$) is 0.3 or more and 0.8 or less.

[0013]

[4] The silicone-release polyester film according to any one of [1] to [3], wherein an alkenyl group of the alkenyl group-containing silicone is a vinyl group.

[0014]

[5] The silicone-release polyester film according to any one of [1] to [4], which is to be used for ceramic green sheet forming in manufacture of a stacked ceramic capacitor.

[0015]

In addition, the present invention provides the following articles to be protected.

[0016]

[6] An article to be protected, wherein the silicone-release polyester film according to any one of [1] to [5] is laminated to the article to be protected on a surface of the coating layer or a surface of the release layer.

[0017]

[7] The article to be protected according to [6], wherein

the article to be protected is a ceramic green sheet.

[0018]

The present invention also provides the following method for manufacturing a silicone-release polyester film.

[0019]

[8] A method for manufacturing a silicone-release polyester film, the method comprising a step of forming a coating layer on at least one side of a polyester film using a coating composition for release including an aqueous dispersion of an alkenyl group-containing silicone, an aqueous dispersion of a silicone having a hydrogen atom directly bonded to a Si atom represented by Si-H group, and an aqueous dispersion containing a platinum-based catalyst, wherein

a platinum element amount in the platinum-based catalyst is more than 120 ppm and less than 600 ppm based on a weight of the alkenyl group-containing silicone;

the platinum-based catalyst includes a platinum-based catalyst containing a crosslinking reaction inhibitor and a platinum-based catalyst containing no crosslinking reaction inhibitor; and

the coating layer has a thickness of 5 nm or more and 70 nm or less.

EFFECT OF THE INVENTION

[0020]

Owing to the configuration described above, the silicone-release polyester film of the present invention is a film having moderately low peeling strength and being superior in uniformity of the release layer. The silicone-release polyester film of the present invention having the characteristics described above can be suitably used, for example, as a carrier film for forming a ceramic green sheet to be used for a stacked ceramic capacitor.

[0021]

In addition, the article to be protected can be suitably used, for example, when a ceramic green sheet is used as the article to be protected since a silicone-release polyester film having the characteristics described above is laminated.

[0022]

The method for manufacturing a silicone-release polyester film of the present invention makes it possible to efficiently and easily obtain a silicone-release polyester film having the characteristics described above.

MODE FOR CARRYING OUT THE INVENTION

[0023]

Hereinafter, a detailed description is made of embodiments of the present invention, but the present

invention is not limited to these embodiments.

[0024]

<Silicone-release polyester film>

The silicone-release polyester film of the present invention is a silicone-release polyester film having, on at least one side of a polyester film, a coating layer formed using a coating composition for release including an aqueous dispersion of an alkenyl group-containing silicone, an aqueous dispersion of a silicone having a hydrogen atom directly bonded to a Si atom represented by Si-H group, and an aqueous dispersion containing a platinum-based catalyst,

wherein

a platinum element amount in the platinum-based catalyst is greater than 120 ppm and less than 600 ppm based on a weight of the alkenyl group-containing silicone;

the platinum-based catalyst includes a platinum-based catalyst containing a crosslinking reaction inhibitor and a platinum-based catalyst containing no crosslinking reaction inhibitor; and

a thickness of the coating layer is 5 nm or more and 70 nm or less.

[0025]

[Polyester film]

For the polyester film of the present invention, known polyesters can be appropriately used, and for

example, those shown below can be suitably used.

[0026]

(Polyester)

The polyester that constitutes a polyester film to be used as the substrate film (hereinafter, sometimes referred to as substrate) in the present invention is not particularly limited, and a film formed product of a polyester commonly used as a substrate for a release film can be used. A crystalline linear saturated polyester composed of an aromatic dibasic acid component and a diol component is preferable. For example, polyethylene terephthalate, polyethylene isophthalate, polyethylene-2,6-naphthalate, polybutylene terephthalate, poly(1,4-cyclohexylenedimethylene terephthalate), polytrimethylene terephthalate, or copolymers containing constituent components of these resins as main components are more preferable. In particular, polyester films formed from polyethylene terephthalate are particularly suitable. In polyethylene terephthalate, the content of repeating units of ethylene terephthalate is preferably 90 mol% or more, more preferably 95 mol% or more, and other dicarboxylic acid components and diol components may be copolymerized in small amounts. For example, from the viewpoint of cost, a copolymer manufactured from only terephthalic acid and ethylene glycol is preferable.

[0027]

Known additives such as an antioxidant, a light stabilizer, an ultraviolet absorber, and a crystallization agent may be added as long as the effect of the release film of the present invention is not impaired. The polyester film is preferably a biaxially oriented polyester film because of its elastic modulus in both directions, and the like.

[0028]

The intrinsic viscosity of the polyester film is preferably 0.50 dl/g or more and 0.70 dl/g or less, and more preferably 0.52 dl/g or more and 0.65 dl/g or less. When the intrinsic viscosity is 0.50 dl/g or more, breakage does not often occur in a stretching step, which is preferable. Conversely, when the intrinsic viscosity is 0.70 dl/g or less, the cuttability of the polyester film at the time of being cut into a predetermined product width is good and dimensional failure does not occur, which is preferable. In addition, it is preferable that the raw material pellets are sufficiently vacuum-dried.

[0029]

In the present specification, the term "polyester film" simply means a polyester film including a surface layer A and a surface layer B (in which the surface layer A and the surface layer B are laminated).

[0030]

The method for manufacturing the polyester film in the present invention is not particularly limited, and methods conventionally commonly used can be used. For example, the polyester film can be obtained by melting the polyester with an extruder, extruding the melted resin into a film form, cooling the extrudate with a rotary cooling drum to obtain an unstretched film, and biaxially stretching the unstretched film. A biaxially stretched film can be obtained by a method in which a film uniaxially stretched in a machine direction or a transverse direction is sequentially stretched biaxially in the transverse direction or the machine direction, or a method in which the unstretched film is simultaneously stretched biaxially in the machine direction and the transverse direction.

[0031]

In the present invention, a stretching temperature when stretching the polyester film is preferably set to be equal to or higher than a secondary transition point (T_g) of the polyester. The polyester film is stretched in each of the machine direction and the transverse direction preferably by once or more and 8 times or less, and particularly preferably by twice or more and 6 times or less.

[0032]

The thickness of the polyester film is preferably 12 μm or more and 100 μm or less, more preferably 16 μm or more and 50 μm or less, and still more preferably 19 μm or more and 33 μm or less. When the thickness of the film is 12 μm or more, there is no risk of deformation due to heat during film production, processing steps, and molding, which is preferable. When the thickness of the film of 100 μm or less, the amount of the film to be disposed after being used is not extremely large, which is preferable for reducing the environmental load.

[0033]

The polyester film substrate may include a single layer or two or more layers. For example, the substrate film may be a polyester film including a surface layer A substantially free of particles having a particle size of 1.0 μm or more and a surface layer B containing particles. Preferably, the surface layer A is substantially free of inorganic particles having a particle size of 1.0 μm or more.

[0034]

In this aspect, particles having a particle size of less than 1.0 μm and 1 nm or more may be present in the surface layer A. The surface layer A is substantially free of particles, for example, inorganic particles, having a particle size of 1.0 μm or more, and therefore the

occurrence of defects due to the transfer of the particle shape in the substrate to the resin sheet can be reduced.

[0035]

In one aspect, the surface layer A does not contain particles having a particle size of less than 1.0 μm , and therefore the occurrence of defects due to the transfer of the particle shape in the substrate to the resin sheet can be suppressed more effectively.

[0036]

In one aspect, the polyester film substrate is preferably a laminated film including a surface layer A substantially free of inorganic particles in at least one surface. This makes it possible to suppress more effectively the occurrence of defects due to the transfer of the particle shape in the substrate to the resin sheet.

[0037]

For example, in a preferred aspect, the surface layer A substantially free of particles having a particle size of less than 1.0 μm is also substantially free of particles having a particle size of 1.0 μm or more.

[0038]

Here, in the present invention, the phrase "substantially free of particles" means, for example, in the case of particles of less than 1.0 μm , a content that is 50 ppm or less, preferably 10 ppm or less, and most

preferably equal to or less than the detection limit when an inorganic element is quantified by fluorescent X-ray analysis. This is because, even if the particles are not positively added into the film, contamination components derived from foreign matters, and dirt attached to raw material resins, or lines or devices in film manufacturing steps may be peeled off and mixed into the film. The phrase "substantially free of particles having a particle size of 1.0 μm or more" means that particles having a particle size of 1.0 μm or more are not positively contained.

[0039]

A laminated polyester film having a multilayer configuration including two or more layers preferably includes a surface layer B that can contain inorganic particles and the like on the opposite surface of the surface layer A substantially free of inorganic particles.

[0040]

As the laminated configuration, when the layer on the side to which the release layer is applied is a layer A, the layer on the opposite surface thereof is a layer B, and the core layer other than these is a layer C, the layer configuration in the thickness direction may be a laminated structure such as release layer/A/B or release layer/A/C/B. As a matter of course, the layer C may have a plurality of

layer configurations. The surface layer B may contain no inorganic particles. In that case, a coating layer containing at least inorganic particles and a binder is preferably provided on the surface layer B in order to impart slipperiness for winding the film into a roll.

[0041]

In the polyester film substrate of the present invention, the surface layer B forming the surface opposite from the surface to which the release layer is applied preferably contains inorganic particles, and especially, silica particles and/or calcium carbonate particles are preferably used from the viewpoint of the slipperiness of the film and the ease of air release. As to the content of inorganic particles contained, the inorganic particles are preferably contained in the surface layer B in an amount of 5000 ppm or more and 15000 ppm or less in total.

[0042]

At this time, the average area surface roughness (S_a) of the film of the surface layer B is preferably in a range of 1 nm or more and 40 nm or less. More preferably, the average area surface roughness is in a range of 5 nm or more and 35 nm or less. When the total content of the silica particles and/or the calcium carbonate particles is 5000 ppm or more, and the S_a is 1 nm or more, air can be uniformly released when the film is wound into a roll, and

the film has a good winding appearance and good flatness, so that the film is suitable for the manufacture of an ultrathin ceramic green sheet. In addition, when the total content of the silica particles and/or the calcium carbonate particles is 15000 ppm or less and the Sa is 40 nm or less, the aggregation of a lubricant is less likely to occur, and coarse protrusions are not formed, so that the quality is stable during the manufacture of the ultrathin ceramic green sheet, which is preferable.

[0043]

As the particles contained in the layer B, inert inorganic particles other than silica and/or calcium carbonate particles and/or heat-resistant organic particles can be used, but silica particles and/or calcium carbonate particles are more preferably used from the viewpoint of transparency and cost. Other examples of the inorganic particles that can be used include alumina-silica composite oxide particles and hydroxyapatite particles. Examples of the heat-resistant organic particles include crosslinked polyacrylic particles, crosslinked polystyrene particles, and benzoguanamine-based particles. When silica particles are used, porous colloidal silica is preferable, whereas when calcium carbonate particles are used, light calcium carbonate surface-treated with a polyacrylic acid-based polymeric compound is preferable from the viewpoint of

preventing the lubricant from falling off.

[0044]

The average particle diameter of the inorganic particles to be added to the surface layer B is preferably 0.1 μm or more and 2.0 μm or less, and particularly preferably 0.3 μm or more and 1.0 μm or less. When the average particle diameter of the inorganic particles is 0.1 μm or more, the slipperiness of the release film is good, which is preferable. When the average particle diameter is 2.0 μm or less, there is no possibility of adversely affecting the smoothness of the surface of the release layer, and therefore there is no possibility of generating pinholes in the ceramic green sheet, which is preferable.

[0045]

In order to improve the adhesion of the release layer or the like to be applied later, or in order to prevent electric charge, a coat layer may be provided on the film before the surface of the surface layer A and/or the surface of the surface layer B are/is subjected to stretching or after being subjected to uniaxial stretching in the film forming process, or the film may be subjected to a corona treatment or the like.

[0046]

[Coating composition for release]

The silicone-release polyester film of the present

invention has a coating layer (release layer) formed using a coating composition for release, and the coating composition for release includes an aqueous dispersion of an alkenyl group-containing silicone, an aqueous dispersion of a silicone having a hydrogen atom directly bonded to a Si atom represented by Si-H group, a platinum-based catalyst containing a crosslinking reaction inhibitor, and a platinum-based catalyst containing no crosslinking reaction inhibitor.

[0047]

The number average molecular weight of the alkenyl group-containing silicone is 10,000 or more and 40,000 or less.

[0048]

The total weight of the platinum element contained as the platinum-based catalysts is 120 ppm or more and 600 ppm or less based on the weight of the alkenyl group-containing silicone.

[0049]

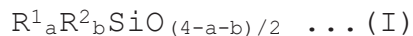
(Alkenyl group-containing silicone)

As the alkenyl group-containing silicone in the present invention, an alkenyl group-containing silicone having a number average molecular weight of 10,000 or more and 40,000 or less is used. Owing to this, the silicone-release polyester film can have superior releasability.

When the number average molecular weight of the alkenyl group-containing silicone is less than the lower limit, the crosslinking reaction rate increases, so that a silicone aggregate is generated. In addition, when the number average molecular weight of the alkenyl group-containing silicone exceeds the upper limit, it becomes difficult to disperse the alkenyl group-containing silicone in water, so that the peeling strength at the peeling rate increases.

[0050]

Examples of the alkenyl group-containing silicone include an organopolysiloxane having a structure represented by the following general formula (I),



in the formula (I),

R^1 is an alkenyl group having 2 to 8 carbon atoms, R^2 is a monovalent saturated hydrocarbon group having 1 to 16 carbon atoms selected from alkyl groups or aryl groups, and

a and b represent integers each satisfying a is 1 to 3, b is 0 to 2, and $a + b \leq 3$.

[0051]

The alkenyl group-containing silicone may have either a linear structure or a branched structure, may be one partly having cross-linking, and may be a mixture thereof. Examples of the alkenyl group having 2 to 8 carbon atoms represented by R^1 include a vinyl group, an allyl group, a

butenyl group, a pentenyl group, and a hexenyl group, and among these groups, a vinyl group is particularly preferable. Examples of the alkyl group represented by R^2 include a methyl group, an ethyl group, a propyl group, and a butyl group, and examples of the aryl group include a phenyl group and a tolyl group. Among them, it is preferable that 80 mol% or more of the substituent of R^2 is a methyl group from the viewpoint of light peelability.

[0052]

From the viewpoint of the curing rate and pot life of the composition, it is preferable that the amount of silicon atoms having an alkenyl group is in the range of 0.05 mol% or more and 20 mol% or less based on the total amount of silicon atoms in the alkenyl group-containing silicone. When the proportion of the silicon atoms having an alkenyl group is less than the lower limit, the curing rate of the composition decreases, and it may be difficult to efficiently form a cured silicone film during the film formation described later. When the proportion of the silicon atoms having an alkenyl group exceeds the upper limit, the pot life of the composition may be shortened.

[0053]

The alkenyl group-containing silicone in the present invention can be produced by a known method. The alkenyl group-containing silicone in the present invention is

contained in the composition in the form of an aqueous dispersion.

[0054]

(Si-H group-containing silicone)

Examples of the silicone having a hydrogen atom directly bonded to a Si atom represented by Si-H group (hereinafter, sometimes referred to as Si-H group-containing silicone) in the present invention include an organohydrogen polysiloxane having a structure represented by the following general formula (II),



in the formula (II),

R^3 is a monovalent saturated hydrocarbon group having 1 to 16 carbon atoms selected from alkyl groups and aryl groups, and

c and d represent integers each satisfying c is 0 to 2, d is 1 to 3, and $c + d \leq 3$.

[0055]

The Si-H group-containing silicone may have either a linear structure or a branched structure. Examples of the alkyl group represented by R^3 include a methyl group, an ethyl group, a propyl group, and a butyl group, and examples of the aryl group include a phenyl group and a tolyl group. Among them, it is preferable that 50 mol% or more of the substituent of R^3 is a methyl group from the

viewpoint of light peelability.

[0056]

From the viewpoint of curing characteristics, the Si-H group-containing silicone preferably has at least three or more, preferably five or more, hydrogen atoms bonded to silicon atoms in one molecule of the silicone.

[0057]

The Si-H group-containing silicone can be produced by a known method. In addition, the Si-H group-containing silicone in the present invention is contained in the composition in the form of an aqueous dispersion.

[0058]

(Ratio of the number of Si-H groups to the number of alkenyl groups)

The ratio of the number of Si-H groups to the number of alkenyl groups (the number of Si-H groups/the number of alkenyl groups) in the coating composition for release in the present invention is preferably in the range of 1.0 or more and 2.0 or less. When the ratio is less than the lower limit, since surplus alkenyl groups remain in the coating layer formed, the peeling strength is likely to change over time, and the crosslinking density decreases, so that the uniformity of peeling force and the residual adhesion rate may be lowered. When the ratio exceeds the upper limit, Si-H groups having high reactivity may remain

in the formed coating layer, so that an increase in peeling force may be caused.

[0059]

(Silicone content)

In the coating composition for release in the present invention, the total of the alkenyl group-containing silicone solid content and the Si-H group-containing silicone solid content is preferably 70% by weight or more based on the solid weight of the composition. Each of the silicone solid contents is more preferably 80% by weight or more and 97% by weight or less. Here, the silicone solid content refers to the amount excluding the aqueous solvent, and the solid weight of the composition refers to the total amount of the solid contents of the respective additives. When the total amount of the silicone solid contents is less than the lower limit, the area covered with silicone is reduced with respect to the film surface on which the coating film is formed, the peeling force is increased, and unevenness may occur in the peeling force.

[0060]

(Aqueous solvent)

As the aqueous solvent for forming each of the aqueous silicone dispersions of the present invention, water is preferably used. By using the aqueous solvent, it is possible to form a silicone release layer without using

an explosion-proof facility and an organic solvent recovery facility required for the organic solvent during the process of manufacturing the release film.

[0061]

(Emulsifier)

Each aqueous silicone dispersion is made using an emulsifier to increase the stability and shear resistance of the aqueous dispersion. As the emulsifier, for example, a nonionic emulsifier that does not affect the curing reaction of the silicone is preferable. An ionic emulsifier may affect the curing reaction of silicone, and may be localized in a coating film, for example, bleed out to the surface to affect releasability.

[0062]

The nonionic emulsifier preferably has an HLB value in the range of 8 or more and 18 or less, and examples thereof include at least one selected from among higher alcohols and alkylene oxide adduct types including alkylene oxide adducts of higher fatty acids, esters of alkylene oxide adducts of higher fatty acids and alcohols, alkylene oxide adducts of alkanolamides, alkylene oxide adducts of sorbitan esters, and alkylene oxide adducts of higher fatty acid glycerides. Here, the HLB value is a value calculated by Griffin's calculation formula.

[0063]

Examples of the alkylene oxide include ethylene oxide, propylene oxide, and butylene oxide, and either one of these or two or more of these may be used. When a plurality of alkylene oxides are used, the type of addition may be either block or random, and the HLB value is preferably in the range of 8 or more and 18 or less, and more preferably in the range of 10 or more and 15 or less. Among these nonionic emulsifiers, polyoxyethylene lauryl ether, polyoxyethylene tridecyl ether, and the like are preferable. When a nonionic emulsifier having an HLB value outside the above range is used as an emulsifier of the aqueous silicone dispersion, the emulsifying and dispersing power and the stability of the aqueous dispersion may be deteriorated.

[0064]

(Catalyst)

In the coating composition for release constituting the coating layer of the present invention, a catalyst is preferably used, and a platinum-based catalyst is particularly preferable in order to make the alkenyl group-containing silicone and the Si-H group-containing silicone undergo an addition reaction. Known platinum-based catalysts can be used, and examples thereof include platinum chloride and chloroplatinic acid. The platinum-based catalyst may be used in a state of being emulsified

using a nonionic emulsifier in advance, or may be used simultaneously when emulsifying silicone. Furthermore, a crosslinking reaction inhibitor described later may be added during emulsification.

[0065]

(Crosslinking reaction inhibitor)

In the present invention, a crosslinking reaction inhibitor is contained in the coating composition for release in order to suppress the activity of the platinum-based catalyst at room temperature. The crosslinking reaction inhibitor is preferably a crosslinking reaction inhibitor having an ethynyl group. When the content of the crosslinking reaction inhibitor is excessively large, the curing reaction of silicone is excessively inhibited, and the formation (crosslinking reaction) of a coating layer becomes difficult. Therefore, the upper limit of the content is not particularly limited as long as the coating layer is formed in consideration of the above matters, but the content is preferably 6 times or less the amount of platinum element. The content is more preferably 5 times or less, and particularly preferably 4 times or less.

[0066]

The crosslinking reaction inhibitor having an ethynyl group is not particularly limited as long as it has an ethynyl group, but since an aqueous coating composition is

adopted in the present invention, it is preferable to use, for example, a crosslinking reaction inhibitor having an ethynyl group and a hydroxyl group typified by 1-ethynylcyclohexanol from the viewpoint of volatility and balance between solubility in water and coordination ability to platinum.

[0067]

(Platinum-based catalyst containing crosslinking reaction inhibitor and platinum-based catalyst containing no crosslinking reaction inhibitor)

In order to efficiently progress the crosslinking reaction, a platinum-based catalyst containing a crosslinking reaction inhibitor and a platinum-based catalyst containing no crosslinking reaction inhibitor are used in combination.

[0068]

Regarding the mechanism for exerting the above-described operation of the present invention, the following assumption is made for the silicone crosslinking reaction of the aqueous dispersion system, but it is not intended to limit the scope of rights of the present invention at all only in the following assumption. In the silicone crosslinking reaction of the aqueous dispersion system, it is presumed that this is a result of a reaction between the polydimethylsiloxane whose emulsion has been broken and the

platinum-based catalyst containing no crosslinking reaction inhibitor occurring in a low temperature region, and a subsequent reaction between the polydimethylsiloxane whose emulsion has been completely broken and the platinum-based catalyst activated by volatilization of the crosslinking reaction inhibitor in the platinum-based catalyst containing a crosslinking reaction inhibitor occurring in a high temperature region.

[0069]

In the present invention, the amount of platinum element in the platinum-based catalysts is more than 120 ppm and less than 600 ppm based on the weight of the alkenyl group-containing silicone, and may be, for example, 130 ppm or more and 550 ppm or less, or more than 150 ppm and 500 ppm or less. Within the above range, the silicone can be sufficiently cured, and a release film superior in light peeling surface property can be obtained.

[0070]

When the weight ratio of platinum element exceeds the above range, the addition reaction between an alkenyl group and an Si-H group is accelerated, and a gelled product of the silicone tends to be generated. When the weight of platinum element is less than 120 ppm, the addition reaction proceeds, but the addition reaction tends to cause poor curing of silicone. From the above viewpoint, the

weight of platinum element is preferably more than 120 ppm.

[0071]

The platinum element amount (P1) of the platinum-based catalyst containing the crosslinking reaction inhibitor in the platinum-based catalyst is preferably 40 ppm or more and less than 400 ppm based on the alkenyl group-containing silicone weight, and may be, for example, 40 ppm or more and 370 ppm or less, 60 ppm or more and 300 ppm or less, or the like.

[0072]

The platinum element amount (P0) of the platinum-based catalyst containing no crosslinking reaction inhibitor in the platinum-based catalyst is preferably 50 ppm or more and less than 400 ppm based on the alkenyl group-containing silicone weight, and may be, for example, 60 ppm or more and 370 ppm or less, 70 ppm or more and 300 ppm or less, or the like.

[0073]

The platinum-based catalyst contains the platinum element amount (P0) of the platinum-based catalyst containing no crosslinking reaction inhibitor and the platinum element amount (P1) of the platinum-based catalyst containing a crosslinking reaction inhibitor, and

the ratio $(P0/(P1 + P0))$ of the platinum element amount (P0) of the platinum-based catalyst containing no

crosslinking reaction inhibitor to the total platinum element weight ($P_1 + P_0$) is preferably 0.3 or more and 0.8 or less, and may be, for example, 0.31 or more and 0.75 or less, and may be, for example, 0.32 or more and 0.70 or less. In particular, since the crosslinking reaction at a low temperature affects the final high crosslinking density, when the platinum element weight ratio of the platinum-based catalyst containing no crosslinking reaction inhibitor is less than 0.3, the crosslinking reaction at a low temperature is not sufficient, so that a film having a high crosslinking density cannot be finally obtained, and the peeling force increases. When the platinum element weight ratio of the platinum-based catalyst containing no crosslinking reaction inhibitor exceeds 0.8, a film having a high crosslinking density is obtained, but since the reaction proceeds immediately after the preparation of the coating liquid, the coating appearance is deteriorated due to gelation of the coating liquid.

[0074]

(Other components)

To the coating composition for release of the present invention may be further added, for example, an agent for imparting adhesiveness to a substrate, a coloring agent, an ultraviolet absorber, particles, or an anti-static agent as long as the object of the present invention is not

impaired.

[0075]

(Preparation of aqueous silicone dispersion)

In preparing each of the aqueous silicone dispersions of the present invention, a method of emulsifying the silicone component, the aqueous solvent, and the emulsifier described above can be employed. A known method can be used for emulsifying these components, and examples thereof include a method in which a silicone prepared in advance, an emulsifier, and other components as necessary are mechanically emulsified in an aqueous medium using a stirring device such as a homogenizer, an Agi Homo Mixer, or an Ultra Planetary Mixer.

[0076]

In addition, the particle size of the aqueous dispersion can be adjusted by adjusting the size of the stirring blade, the stirring speed, and the stirring time. The average particle diameter of each of the aqueous silicone dispersions of the present invention is preferably 200 nm or less, and more preferably 100 nm or more and 200 nm or less.

[0077]

[Coating layer]

In the present invention, a coating layer (release layer) is formed on at least one surface of a polyester

film using the coating composition for release of the present invention. The coating layer (release layer) of the present invention is formed by applying the coating composition for release onto the polyester film, and then drying it.

[0078]

In the present invention, the thickness of the coating layer is preferably 5 nm or more and 70 nm or less in terms of a thickness after drying. When the thickness of the coating layer is less than the lower limit, the release characteristics may be insufficient, and when the thickness exceeds the upper limit, the peeling strength increases, and it is necessary to increase the concentration of the coating liquid or to increase the coating amount, so that it tends to be difficult to perform coating.

[0079]

When the coating composition for release of the present invention is applied onto a polyester film, an aqueous coating liquid containing the composition is prepared, and the solid concentration of the aqueous coating liquid is preferably 20% by weight or less, more preferably 1% by weight or more and 10% by weight or less based on the weight of the coating liquid. When the solid concentration in the aqueous coating liquid is less than

the lower limit, the wettability to the polyester film may be insufficient. When the solid concentration exceeds the upper limit, the stability of the coating liquid and the appearance of the coating layer may be deteriorated. Water is preferably used as the aqueous solvent for adjusting the solid concentration.

[0080]

The aqueous coating liquid can be applied to the polyester film at any stage, but is preferably applied in the process of producing the polyester film, and is preferably applied to the polyester film before oriented crystallization is completed.

[0081]

Here, the polyester film before oriented crystallization is completed orientation includes an unstretched film, a uniaxially oriented film obtained by orienting an unstretched film in either the machine direction (hereinafter, this direction may be referred to as a continuous film formation direction, a machine direction, or an MD direction) or the transverse direction (hereinafter, this direction may be referred to as a direction orthogonal to the machine direction, a transverse direction, or a TD direction), and a film obtained by subjecting an unstretched film to a low stretch orientation in two directions, namely, the machine direction and the

transverse direction (a biaxially stretched film obtained before the film is finally restretched in the machine direction or the transverse direction to complete oriented crystallization). Among them, preferred is so-called in-line coating, in which an aqueous coating liquid of the composition described above is applied to an unstretched film or a uniaxially stretched film oriented in one direction, and stretching in the machine direction and/or stretching in the transverse direction and heat fixation are immediately performed. The coating layer may be dried by the stretching step or the heat fixation treatment after the coating, and a drying step may be further added, as necessary. When the composition is cured using a catalyst to obtain a cured film, the composition may be cured by the stretching step or the heat fixation treatment, but a curing step may be further added, as necessary.

[0082]

When the aqueous coating liquid is applied to the polyester film, for example, it is preferable to subject the film surface to a physical treatment, such as a corona surface treatment, a flame treatment, or a plasma treatment, as a preliminary treatment for improving coatability, or to use the above-described emulsifier as a wetting agent together with the composition.

[0083]

As an application method, any known coating method can be applied. For example, a roll coating method, a gravure coating method, a roll brushing method, a spray coating method, an air knife coating method, an impregnation method, a curtain coating method, and the like may be used alone or in combination.

[0084]

<Method for manufacturing silicone-release polyester film>

The method for manufacturing a silicone-release polyester film of the present invention is a method for manufacturing a silicone-release polyester film, the method comprising a step of forming a coating layer on at least one side of a polyester film using a coating composition for release including an aqueous dispersion of an alkenyl group-containing silicone, an aqueous dispersion of a silicone having a hydrogen atom directly bonded to a Si atom represented by Si-H group, and an aqueous dispersion containing a platinum-based catalyst, wherein

a platinum element amount in the platinum-based catalyst is more than 120 ppm and less than 600 ppm based on a weight of the alkenyl group-containing silicone;

the platinum-based catalyst includes a platinum-based catalyst containing a crosslinking reaction inhibitor and a platinum-based catalyst containing no crosslinking reaction inhibitor; and

the coating layer has a thickness of 5 nm or more and 70 nm or less.

[0085]

The method for manufacturing a silicone-release polyester film of the present invention makes it possible to efficiently and easily obtain a silicone-release polyester film having the characteristics described above. Note that the manufacturing method described below is an example, and the present invention is not limited thereto.

[0086]

In the manufacturing method, for each configuration, the description regarding the silicone-release polyester film and the like in the present specification can be applied appropriately.

[0087]

As the step of forming the coating layer using the coating composition for release of an aqueous dispersion in the manufacturing method, a known method can be appropriately used as long as it is a method of forming the coating layer on the film using the coating composition for release of an aqueous dispersion.

[0088]

<Article to be protected>

In the article to be protected of the present invention, the silicone-release polyester film described

above is laminated with the article on a surface of the coating layer or a surface of the release layer.

[0089]

Examples of the article to be protected include an organic resin sheet, an inorganic resin sheet, a glass plate, a metal plate, a ceramic sheet, and an adhesive sheet. The article to be protected of the present invention can be suitably used, for example, when a ceramic green sheet is used as the article to be protected since the silicone-release polyester film having the characteristics described above is laminated.

EXAMPLES

[0090]

The present invention will be described specifically by way of Examples, but the present invention is not limited to the following Examples. Physical properties and characteristics in Examples were measured or evaluated by the following methods. The indication with "part" means "part by mass".

[0091]

Each measurement, evaluation, and the like in Examples were performed as follows.

[0092]

(1) Peelability of ceramic sheet

90 parts by weight of barium titanate (BaTiO_3), 7 parts by weight of polyvinyl butyral, 1.5 parts by weight of dioctyl phthalate, and 2.5 parts by weight of a polycarboxylic acid-based polymer surfactant were added to a mixed solvent of toluene : ethanol =1 : 1 (volume ratio), and dispersed with a ball mill to prepare a slurry. The slurry was uniformly applied onto a coating layer (release layer) of a release polyester film such that the thickness after drying was 2 μm , and then dried to form a ceramic sheet.

[0093]

The release polyester film on which the ceramic sheet was formed was cut into a size of 25 mm × 150 mm, and an adhesive tape (trade name "31B Tape" manufactured by Nitto Denko Corporation) was bonded to the ceramic sheet side to prepare a test piece. The test piece was subjected to humidity control under conditions of 23°C and a humidity of 50% for 24 hours, and then the ceramic sheet (31B tape side) was peeled off at a peeling angle of 90° and a peeling rate of 10 m/min using a tensile tester, and the peeling strength was measured.

[0094]

For the peeling strength of the ceramic sheet, superiority and inferiority were determined according to the following indexes.

O: The peeling strength is 0.60 g/25 mm or less.

X: The peeling strength is more than 0.60 g/25 mm.

[0095]

(2) Residual adhesion rate

The peeling strength after bonding a polyester adhesive tape (No. 31B manufactured by Nitto Denko Corporation) to a cold-rolled stainless steel plate (SUS304) specified in JIS G 4305 was measured and taken as the basic adhesive force (f_0). In addition, the polyester adhesive tape was pressure-bonded to the surface of the release layer of the release polyester film with a pressure roller weighing 5 kg and maintained for 30 seconds, the adhesive tape was then peeled off, and the peeling strength after the peeled adhesive tape was attached to the stainless steel plate was measured and taken as the residual adhesive force (f). From the basic adhesive force (f_0) and the residual adhesive force (f) obtained, a residual adhesion rate was determined using the following formula. The peeling angle was 180 degrees, and the peeling rate was 300 mm/min.

$$\text{Residual adhesion rate (\%)} = (f)/(f_0) \times 100$$

The residual adhesion rate is preferably 90% or more, which indicates that the silicone crosslinking density is high. When the residual adhesion rate is less than 90%, this indicates that crosslinking is insufficient.

[0096]

(3) Coating layer thickness

A film was fixed with an embedding resin, a section of the film was cut with a microtome such that the section of the film could be observed, and the film was stained with 2% osmium acid at 60°C for 2 hours and observed using a transmission electron microscope (JEM2010 manufactured by JEOL Ltd.), and the thickness of the release layer was measured.

[0097]

(4) Application uniformity

The application uniformity of the release layer was evaluated according to the following criteria by visually observing the surface of the release layer under reflected light.

◎: There is no application defect, and the application is very uniform.

○: There is no application defect, but rainbow-patterned irregularities are slightly observed in the machine direction.

△: Fine application defects and application streaks in the machine direction are slightly observed.

×: Fine application defects frequently occur, and clear application streaks are observed in the machine direction, which cannot be said to be uniform application.

[0098]

[Examples 1 to 5, Comparative Examples 1 to 8]

Molten polyethylene terephthalate ($[\eta] = 0.64 \text{ dl/g}$, $T_g = 78^\circ\text{C}$) containing 0.1% by mass of calcium carbonate particles having an average particle diameter of $0.7 \text{ }\mu\text{m}$ was extruded from a die, cooled with a cooling drum by a conventional method to form an unstretched film, which was subsequently stretched 3.6 times in the machine direction. Then, an aqueous coating liquid (aqueous dispersion having a solid concentration of 5% by mass) prepared by mixing the components to have the solid content ratio given in Table 1 was uniformly applied to the surface of the film with a roll coater to form a coating layer (release layer) such that the coating thickness after drying was 30 nm.

[0099]

Subsequently, this coated film was dried at 115°C over about 5 seconds, stretched 4.5 times in the transverse direction at 145°C , and further heat-fixed at 230°C for about 5 seconds, affording a 25 μm biaxially stretched polyester film having the coating layer (release layer) shown in Table 1.

[0100]

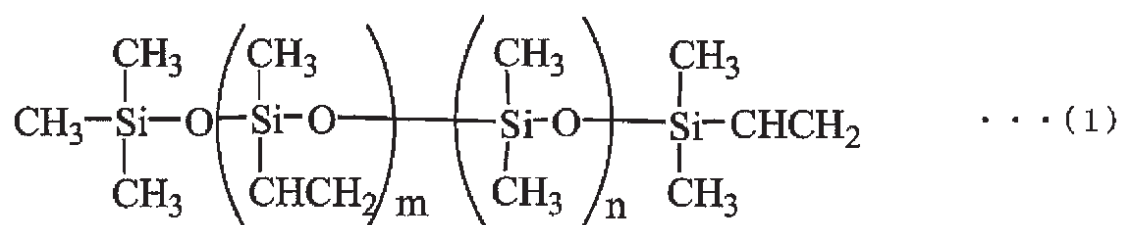
<Aqueous alkenyl group-containing silicone dispersion>

Using an emulsifying device (manufactured by N.P. Labo Co., Ltd., device name: "Ultra Planetary Mixer")

capable of stirring the entire container, a raw material composed of 98% by weight of a silicone having an alkenyl group represented by the following formula (1) (number average molecular weight: 28000) and 2% by weight of polyoxyethylene lauryl ether (manufactured by Kao Corporation, trade name: "EMULGEN 109P") as a surfactant was mechanically emulsified in an aqueous medium, affording an aqueous alkenyl group-containing silicone dispersion having a solid content of 20% by weight. In addition, the emulsion particle diameter was adjusted by adjusting the stirring speed and the stirring time at the time of emulsification.

[0101]

[Formula 1]



(In the formula (1), m was 2, and n was adjusted such that the number average molecular weight was 28000.)

[0102]

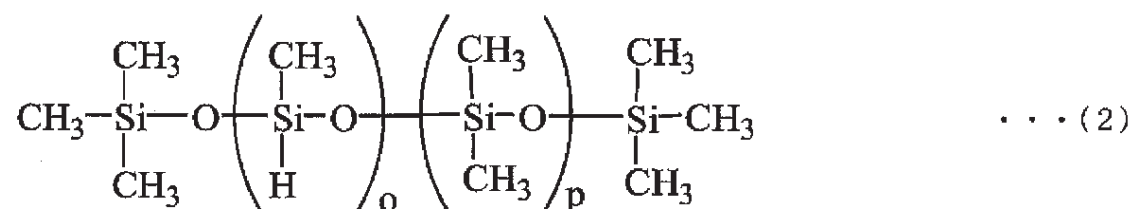
<Aqueous Si-H group-containing silicone dispersion>

Using an emulsifying device (manufactured by N.P. Labo Co., Ltd., device name: "Ultra Planetary Mixer") capable of stirring the entire container, a raw material

composed of 98% by weight of a silicone having a hydrogen group represented by the following formula (2) (number average molecular weight: 5000) and 2% by weight of polyoxyethylene lauryl ether (manufactured by Kao Corporation, trade name: "EMULGEN 109P") as a surfactant was mechanically emulsified in an aqueous medium, affording an aqueous Si-H group-containing silicone dispersion having a solid content of 20% by weight. In addition, the emulsion particle diameter was adjusted by adjusting the stirring speed and the stirring time at the time of emulsification.

[0103]

[Formula 2]



(In the formula (2), o = 40 and p = 35.)

[0104]

<Platinum-based catalyst>

A platinum-based catalyst (P1) containing a reaction inhibitor: an aqueous dispersion having a solid content of 10% by weight was prepared using a solution of chloroplatinic acid in isopropyl alcohol (an amount at which platinum metal was contained at 500 ppm by mass in

the present composition), 99.75% by weight of polyoxyethylene lauryl ether (manufactured by Kao Corporation, trade name: "EMULGEN 109P") as a surfactant, 0.2% by weight of a crosslinking reaction inhibitor (1-ethynylcyclohexanol), and pure water. In the platinum-based catalyst (P1), the crosslinking reaction inhibitor is preferentially coordinated, so that the catalytic effect can be delayed until the reaction inhibitor volatilizes.

[0105]

A platinum-based catalyst (P0) containing no reaction inhibitor: an aqueous dispersion was prepared using a solution of chloroplatinic acid in isopropyl alcohol (an amount at which platinum metal was contained at 500 ppm by mass in the present composition), 99.95% by weight of polyoxyethylene lauryl ether (manufactured by Kao Corporation, trade name: "EMULGEN 109P") as a surfactant, and pure water. Since the platinum-based catalyst (P0) contains no reaction inhibitor, a catalytic effect can be exhibited from a low temperature range.

[0106]

<Adjustment of silicone coating liquid>

A coating liquid was prepared by using, as a coating composition for release, a composition composed of 90 parts by weight of an aqueous alkenyl group-containing silicone dispersion/10 parts by weight of an aqueous Si-H group-

containing silicone dispersion/a platinum-based catalyst (the addition amount was adjusted such that the platinum element amount $P_0 + P_1$ was as indicated in Table 1), and diluting the composition with water to a solid concentration of the coating liquid of 5% such that a target coating layer thickness would be attained.

[0107]

The formulation and the results are shown in Table 1.

[0108]

[Table 1]

		Example 1	Example 2	Example 3	Example 4	Example 5	Compara tive Example 1	Compara tive Example 2	Compara tive Example 3	Compara tive Example 4	Compara tive Example 5	Compara tive Example 6	Compara tive Example 7	Compara tive Example 8
Platinum element weight (P0 + P1) relative to vinyl group- containing silicone amount	ppm	160	160	160	500	500	700	700	100	100	160	160	500	500
Platinum element weight (P0) containing no crosslinking reaction inhibitor	ppm	51	72	112	160	350	700	0	100	0	160	0	500	0
Platinum element weight (P1) containing crosslinking reaction inhibitor	ppm	109	88	48	340	150	0	700	0	100	0	160	0	500
Platinum element weight ratio (P0)/(P0 + P1) containing no crosslinking reaction inhibitor	-	0.32	0.45	0.7	0.32	0.7	1	0	1	0	1	0	1	0
Peeling force	mN/ mm	0.52	0.48	0.49	0.45	0.43	0.43	0.48	0.69	0.75	0.56	0.63	0.46	0.49
Residual adhesion rate	%	96	98	98	98	98	98	98	84	83	95	92	98	98
Coating appearance	-	⊙	⊙	⊙	○	△ to ○	×	×	⊙	⊙	○	⊙	×	△

[0109]

As can be seen from Table 1, the films of Examples of the present invention were superior in peelability, residual adhesion rate, and appearance. This is because a film with a very high crosslinking density was obtained by combining a catalyst containing a crosslinking reaction inhibitor and a catalyst containing no crosslinking reaction inhibitor. On the other hand, in Comparative Examples 1 and 2, a gelled state occurred due to the excessively large total amounts of platinum element, and the coating appearance was also poor. In Comparative Examples 3 and 4, poor results were obtained due to the excessively small total amounts of platinum element. In Comparative Example 5, since the crosslinking reaction from a low temperature region progressed a lot, the effective amount of platinum element in a high temperature region decreased, the crosslinking density finally decreased, and the peeling force increased. In Comparative Example 6, the effective platinum element amount in a low temperature region decreased, so that the crosslinking reaction in the low temperature region did not proceed and only the crosslinking reaction in the high temperature region occurred. As a result, the crosslinking density decreased and the peeling force increased. In Comparative Example 7, the total amount of platinum element was large, so that the

crosslinking reaction proceeded excessively from a low temperature region and the coating appearance was also poor. In Comparative Example 8, the total amount of platinum element was large, so that the crosslinking reaction only in a high temperature region proceeded excessively and the coating appearance was also poor.

CLAIMS

1. A silicone-release polyester film having, on at least one side of a polyester film, a coating layer formed using a coating composition for release including an aqueous dispersion of an alkenyl group-containing silicone, an aqueous dispersion of a silicone having a hydrogen atom directly bonded to a Si atom represented by Si-H group, and an aqueous dispersion containing a platinum-based catalyst, wherein

a platinum element amount in the platinum-based catalyst is greater than 120 ppm and less than 600 ppm based on a weight of the alkenyl group-containing silicone; the platinum-based catalyst includes a platinum-based catalyst containing a crosslinking reaction inhibitor and a platinum-based catalyst containing no crosslinking reaction inhibitor; and

a thickness of the coating layer is 5 nm or more and 70 nm or less.

2. The silicone-release polyester film according to claim 1, wherein

a platinum element amount (P0) of the platinum-based catalyst containing no crosslinking reaction inhibitor is 50 ppm or more and less than 400 ppm based on the weight of

the alkenyl group-containing silicone, and

a platinum element amount (P1) of the platinum-based catalyst containing a crosslinking reaction inhibitor is 40 ppm or more and less than 400 ppm based on the weight of the alkenyl group-containing silicone.

3. The silicone-release polyester film according to claim 1 or 2, wherein

the platinum-based catalyst contains a platinum element amount (P0) of the platinum-based catalyst containing no crosslinking reaction inhibitor and a platinum element amount (P1) of the platinum-based catalyst containing a crosslinking reaction inhibitor, and

a ratio $(P0/(P1 + P0))$ of the platinum element amount (P0) of the platinum-based catalyst containing no crosslinking reaction inhibitor to a total platinum element weight $(P1 + P0)$ is 0.3 or more and 0.8 or less.

4. The silicone-release polyester film according to any one of claims 1 to 3, wherein an alkenyl group of the alkenyl group-containing silicone is a vinyl group.

5. The silicone-release polyester film according to any one of claims 1 to 4, which is to be used for ceramic green sheet forming in manufacture of a stacked ceramic

capacitor.

6. An article to be protected, wherein the silicone-release polyester film according to any one of claims 1 to 5 is laminated to the article to be protected on a surface of the coating layer or a surface of the release layer.

7. The article to be protected according to claim 6, wherein the article to be protected is a ceramic green sheet.

8. A method for manufacturing a silicone-release polyester film, the method comprising a step of forming a coating layer on at least one side of a polyester film using a coating composition for release including an aqueous dispersion of an alkenyl group-containing silicone, an aqueous dispersion of a silicone having a hydrogen atom directly bonded to a Si atom represented by Si-H group, and an aqueous dispersion containing a platinum-based catalyst, wherein

a platinum element amount in the platinum-based catalyst is more than 120 ppm and less than 600 ppm based on a weight of the alkenyl group-containing silicone;

the platinum-based catalyst includes a platinum-based catalyst containing a crosslinking reaction inhibitor and a

platinum-based catalyst containing no crosslinking reaction inhibitor; and

the coating layer has a thickness of 5 nm or more and 70 nm or less.