

DESCRIPTION

TITLE OF THE INVENTION: RELEASE FILM

TECHNICAL FIELD

[0001]

The present invention relates to a release film including a substrate film and a release layer, and relates to a release film useful as a film for various processes.

BACKGROUND ART

[0002]

Conventionally, a release film including a polyester film or the like as a substrate has high heat resistance and mechanical properties, and is used as a process film for forming a resin sheet such as a pressure-sensitive adhesive sheet, a cover film, a ceramic slurry, or a polymer electrolyte film. As a release layer of the release film, many release layers formed of a coating composition containing silicone have been proposed because of good heat resistance and peelability (for example, Patent Documents 1 to 7).

[0003]

Patent Documents 1 and 2 propose a release film in which a release layer is formed of a coating composition containing a polysiloxane having an unsaturated group, a

polysiloxane having an Si-H group, a platinum group metal-based catalyst and the like, and an organic solvent.

[0004]

However, this technique provides an organic solvent-based coating composition, and thus has a problem that the technique is not suitable for a method for applying the composition while a substrate film is stretched and formed (hereinafter, referred to as "in-line coating"). That is, since the organic solvent is used alone as the solvent of the coating composition, large-scale explosion-proof facilities are required for facilities for film-forming and stretching, and there is a problem that the initial installation cost for the facilities is required and the operation of the facilities is complicated, so that the manufacturing cost is increased.

[0005]

Meanwhile, Patent Document 3 proposes a release film in which a release layer is formed using an aqueous coating composition containing an alkenyl group-containing silicone and an Si-H group-containing silicone as a technique suitable for in-line coating. As Examples, a release film is disclosed, in which a release layer is formed using an alkenyl group-containing silicone having a number average molecular weight of 25,000 and an Si-H group-containing silicone having a number average molecular weight of 4,500.

[0006]

Patent Document 4 proposes a release film in which a release layer is formed using an aqueous coating composition containing an alkenyl group-containing silicone having a Q unit represented by $\text{SiO}_{4/2}$ and an Si-H group-containing silicone for the purpose of achieving both light peelability and good wettability. As Examples, a release film is disclosed, in which a release layer is formed using an alkenyl group-containing silicone having a Q unit and having a number average molecular weight of 25,000 and an Si-H group-containing silicone having a number average molecular weight of 4,500.

[0007]

As described above, conventionally, a relatively high molecular weight unsaturated group-containing polysiloxane has been generally used so that the helical structure of polydimethylsiloxane is easily formed on the surface of a coating film when a release layer is formed. The same applies to the case of using an organic solvent-based coating composition (for example, Patent Documents 1 and 2).

[0008]

Meanwhile, Patent Document 5 proposes a release film using polyvinyl alcohol as a primer layer of a release layer of a silicone resin. The primer layer is formed in a

coating step different from that of the release layer, and two coats are required before the release film is produced. Usually, after the primer layer is applied, the release film is wound up as a film roll, and then the film roll is unwound at another processing place to apply the release layer, so that the number of management items increases, and the manufacturing process becomes complicated, which is not efficient.

[0009]

Patent Document 6 proposes a technique for forming a release layer by adding a polyvinyl alcohol-based resin to an aqueous coating composition containing an addition reaction type silicone for the purpose of adjusting the peelability of the release layer. However, as the addition reaction type silicone, those having a relatively high molecular weight have been used as in other Patent Documents.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0010]

Patent Document 1: JP-A-2003-292894

Patent Document 2: JP-A-2003-292895

Patent Document 3: JP-B-6077327

Patent Document 4: JP-A-2021-11081

Patent Document 5: JP-A-2000-289168

Patent Document 6: JP-B-5319329

Patent Document 7: WO2017/200056

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0011]

However, in recent years, a member such as a ceramic green sheet formed on a release layer of a release film tends to be thinned, and the surface of the release layer may be required to have not only peelability but also wettability to a ceramic slurry or the like, which makes it difficult to achieve both of them. That is, when the chemical composition of the release layer is changed in order to enhance the wettability, there is a problem that the peelability is deteriorated.

[0012]

Patent Document 7 proposes a release film including a release layer made of an organic solvent-based coating composition containing a polydimethylsiloxane having a vinyl group with a molecular weight of 500 to 30,000 and a polydimethylsiloxane having an Si-H group with a molecular weight of 150 to 10,000. However, it is not suggested to achieve both peelability and wettability, and there is a problem that the release film is not suitable for in-line

coating because of the organic solvent-based coating composition.

[0013]

According to the study of the present inventors, it has been found that when a silicone-based release film is recycled and used as a raw material of a substrate film, foreign matters of a specific size or more are generated depending on the composition of the release layer, and thus the silicone-based release film is not suitable for recycling.

[0014]

According to another study by the present inventors, it has been found that when a release layer is formed using a silicone-based aqueous coating composition, the influence of aggregates generated at the time of applying the release layer on the surface shape tends to be a problem in coping with thinning of a ceramic green sheet or the like.

[0015]

Therefore, an object of the present invention is to provide a release film which easily achieves both peelability and wettability of a release layer and has good coating uniformity and recyclability of the release layer.

MEANS FOR SOLVING THE PROBLEMS

[0016]

As a result of intensive studies to solve such problems, the present inventors have found that the above problems can be solved by forming a release layer using an aqueous coating composition using a silicone having a lower molecular weight than before, and have completed the present invention. That is, the present invention includes the following contents.

[0017]

[1] A release film comprising: a substrate film; and a release layer formed by reacting and solidifying an aqueous coating composition, in which the aqueous coating composition contains an alkenyl group-containing silicone which has two or more alkenyl groups in a molecule, may have a Q unit represented by $\text{SiO}_{4/2}$, and has a number average molecular weight of 1000 or more and less than 10,000, and an Si-H group-containing silicone having two or more Si-H groups in a molecule and having a number average molecular weight of 1,000 or more and 5,000 or less.

[2] The release film according to [1], in which the aqueous coating composition contains a polyvinyl alcohol-based resin.

[0018]

[3] The release film according to [2], in which the polyvinyl alcohol-based resin has a viscosity of 5 mPa·s or more and 50 mPa·s or less, when an aqueous solution having

a concentration of 4% by mass is measured at a temperature of 20°C, and has a degree of saponification of 85 mol% or more and 99 mol% or less

[0019]

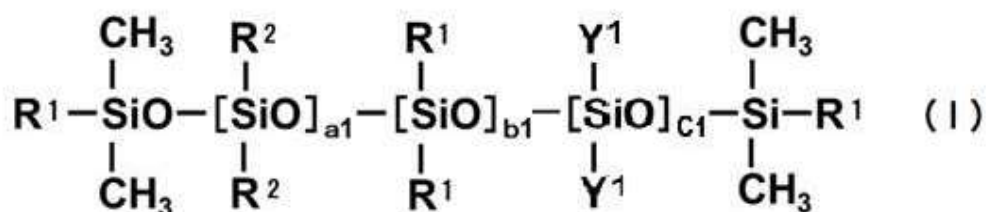
[4] The release film according to any one of [1] to [3], in which the alkenyl group-containing silicone has a Q unit represented by $\text{SiO}_{4/2}$.

[0020]

[5] The release film according to any one of [1] to [4], in which the alkenyl group-containing silicone is represented by the following general formula (I):

[0021]

[Formula 1]



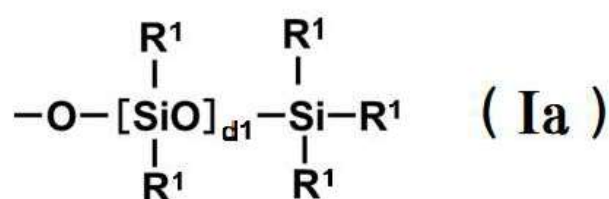
[0022]

in which R^1 is an alkenyl group having 2 or more and 8 or less carbon atoms or a monovalent hydrocarbon group having 1 or more and 16 or less carbon atoms and containing an alkyl group or an aryl group, which may be the same or different; one or more of R^1 bonded to a silicon atom represented by $[\text{SiO}]_{b1}$ are an alkenyl group having 2 or more and 8 or less carbon atoms; R^2 is a monovalent

hydrocarbon group having 1 or more and 16 or less carbon atoms and containing an alkyl group or an aryl group, which may be the same or different; Y¹ is represented by the general formula (Ia) which may be the same or different;

[0023]

[Formula 2]



[0024]

in which R¹ is the same as R¹ in the general formula (I), and may be the same or different;

in the entire general formula (I) including Y¹, when a content of all silicon atoms including terminals is 100 mol%, a content of a1 is 50 mol% or more and 98 mol% or less, a content of b1 is 0 mol% or more and 10 mol% or less, a content of c1 is 0 mol% or more and 30 mol% or less, and a content of d1 is 0 mol% or more and 50 mol% or less; and

in the entire general formula (I) including Y¹, two or more of R¹ are alkenyl groups having 2 or more and 8 or less carbon atoms.

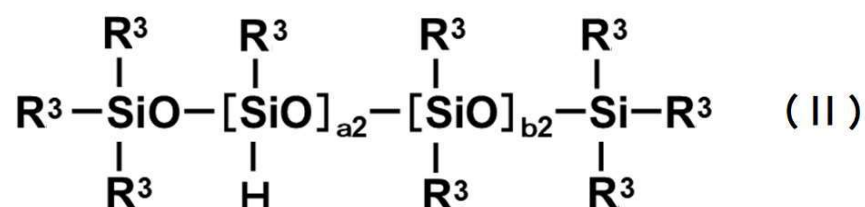
[0025]

[6] The release film according to any one of [1] to [5], in which the Si-H group-containing silicone is

represented by the following general formula (II):

[0026]

[Formula 3]



[0027]

in which R³ is a monovalent hydrocarbon group having 1 or more and 16 or less carbon atoms and containing an alkyl group or an aryl group, which may be the same or different; and

when a content of a₂ + b₂ is 100 mol%, a content of a₂ is 30 mol% or more and 90 mol% or less, and a content of b₂ is 10 mol% or more and 70 mol% or less.

[0028]

[7] The release film according to any one of [1] to [6], in which the aqueous coating composition contains 1 part by mass or more and 50 parts by mass or less of the Si-H group-containing silicone with respect to 100 parts by mass of the alkenyl group-containing silicone.

[0029]

[8] The release film according to any one of [1] to [7], in which the release layer is formed by applying the aqueous coating composition to the substrate film before

completion of crystal orientation, stretching the substrate film in at least one direction, and then subjecting the substrate film to a heat treatment to complete the crystal orientation.

[0030]

[9] The release film according to any one of [1] to [8], in which the substrate film is a polyester film.

[0031]

[10] The release film according to any one of according to any one of [1] to [9], in which the release film is a release film for a multilayer ceramic capacitor or a release film for a resin sheet.

EFFECT OF THE INVENTION

[0032]

According to the present invention, it is possible to provide a release film which easily achieves both peelability and wettability of a release layer and has good coating uniformity and recyclability of the release layer.

[0033]

Although the details of the reason why such an effect can be obtained are not clear, it is considered that since a silicone crosslinked body in which silicones having a relatively low molecular weight react with each other easily forms a dense three-dimensional structure, the

hardness is easily maintained even in a state of being in contact with an organic solvent, and an adhesive force at the time of peeling off a laminate applied and cast on the surface of the release layer can be reduced. The silicone-crosslinked body having the dense three-dimensional structure is less likely to form a helical structure such as polydimethylsiloxane. This is considered to affect the surface free energy of the surface of the release layer, so that moderate wettability with respect to the laminate is easily exhibited. It is considered that when the aqueous coating composition contains the polyvinyl alcohol-based resin, the wettability of the release layer can be improved while the peelability of the release layer is maintained.

[0034]

Furthermore, it is considered that by reducing the molecular weight of the silicone contained in the aqueous coating composition, the stability and uniformity of the coating film are increased, an aggregate hardly occurs in the release layer, and the coating uniformity is improved. It is considered that even when the coating film is remelted during recycling, the coating film is highly uniform, and thus the silicone is easily dispersed in a substrate film resin in which coating films are remelted, so that foreign matters are less likely to be generated.

[0035]

In particular, it is considered that when the alkenyl group-containing silicone has the Q unit, which makes it easier to form a dense three-dimensional structure, and makes it easy to achieve both peelability and wettability of the release layer.

MODE FOR CARRYING OUT THE INVENTION

[0036]

Hereinafter, the present invention will be described in detail.

[0037]

[Release film]

A release film of the present invention includes a substrate film (hereinafter, sometimes referred to as a "substrate") and a release layer formed by reacting and solidifying an aqueous coating composition. As will be described in detail later, since the aqueous coating composition contains two types of silicones that can react with each other, it is not easy to identify the structure of the resulting polymer and specify the claims based on the structure, and there are unrealistic circumstances. Therefore, the release film of the present invention was specified in the form of product-by-process claims.

[0038]

[Release layer]

The release layer is obtained by reacting and solidifying the aqueous coating composition. The aqueous coating composition contains an alkenyl group-containing silicone which has two or more alkenyl groups in a molecule, may have a Q unit represented by $\text{SiO}_{4/2}$, and has a number average molecular weight of 1,000 or more and less than 10,000, and an Si-H group-containing silicone which has two or more Si-H groups in a molecule and has a number average molecular weight of 1000 or more and 5000 or less. The aqueous coating composition may contain a polyvinyl alcohol-based resin. Hereinafter, each component will be described in detail.

[0039]

(Alkenyl group-containing silicone)

As the alkenyl group-containing silicone, an alkenyl group-containing silicone which has two or more alkenyl groups in a molecule and has a Q unit represented by $\text{SiO}_{4/2}$ and/or an alkenyl group-containing silicone which has two or more alkenyl groups in a molecule and does not have a Q unit represented by $\text{SiO}_{4/2}$ can be used.

[0040]

The alkenyl group-containing silicone which has a Q unit may be any compound as long as the alkenyl group-containing silicone has two or more alkenyl groups and a Q unit represented by $\text{SiO}_{4/2}$ in a molecule and has a siloxane

bond in a main chain, but a polyorganosiloxane which has an alkenyl group at a terminal and/or a side chain is preferable. A copolymer containing a dialkylsiloxane unit or an alkylphenylsiloxane unit is preferable because it is easy to adjust the amount of alkenyl groups in one molecule while exhibiting peelability. A silicon atom at the terminal preferably has an alkenyl group, but may have a trialkylsilane structure such as trimethylsilane.

[0041]

The alkenyl group-containing silicone which does not have a Q unit may be any compound as long as the alkenyl group-containing silicone has two or more alkenyl groups in a molecule and has a siloxane bond in a main chain, but a polyorganosiloxane which has an alkenyl group at a terminal and/or a side chain is preferable. A copolymer containing a dialkylsiloxane unit or an alkylphenylsiloxane unit is preferable because it is easy to adjust the amount of alkenyl groups in one molecule while exhibiting peelability. A silicon atom at the terminal preferably has an alkenyl group, but may have a trialkylsilane structure such as trimethylsilane.

[0042]

In any alkenyl group-containing silicone, the alkenyl group may be introduced into any of one terminal, both terminals, and a side chain, but it is preferable that the

alkenyl group is introduced into at least any one terminal, and it is more preferable that the alkenyl group is introduced into each of both terminals of the main chain. The number of the alkenyl groups is 2 or more, preferably 2 or more and 20 or less, and more preferably 2 or more and 10 or less in the molecule.

[0043]

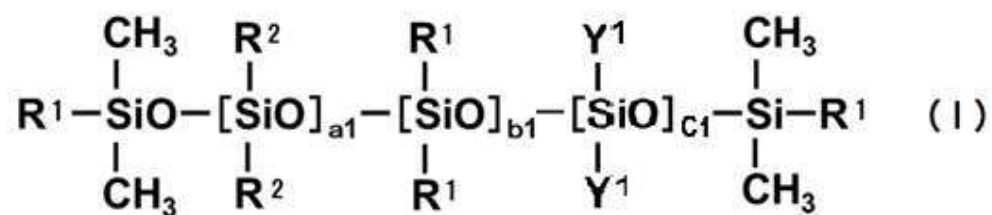
In the case of the alkenyl group-containing silicone having a Q unit, the content of the Q unit represented by $\text{SiO}_{4/2}$ is preferably 0.5 mol% or more and 30 mol% or less, and more preferably 0.5 mol% or more and 20 mol% or less when the content of all silicon atoms including terminals in the molecule is 100 mol%. When the content of the Q unit is 0.5 mol% or more, it becomes easy to form a dense release layer having a high cohesive force, and it becomes easy to achieve both peelability and wettability of the release layer. When the content of the Q unit is 30 mol% or less, excessive formation of a dense structure is suppressed, and brittleness of the coating film is easily suppressed.

[0044]

Examples of the alkenyl group-containing silicone include an organopolysiloxane represented by the following general formula (I):

[0045]

[Formula 4]

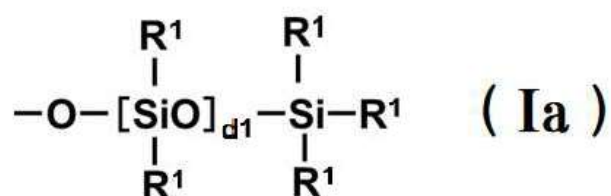


[0046]

in which R¹ is an alkenyl group having 2 or more and 8 or less carbon atoms or a monovalent hydrocarbon group having 1 or more and 16 or less carbon atoms and containing an alkyl group or an aryl group, which may be the same or different; one or more of R¹ bonded to a silicon atom represented by [SiO]_{b1} are an alkenyl group having 2 or more and 8 or less carbon atoms; R² is a monovalent hydrocarbon group having 1 or more and 16 or less carbon atoms and containing an alkyl group or an aryl group, which may be the same or different; and Y¹ is represented by the general formula (Ia) which may be the same or different;

[0047]

[Formula 5]



[0048]

in which R¹ is the same as R¹ in the general formula

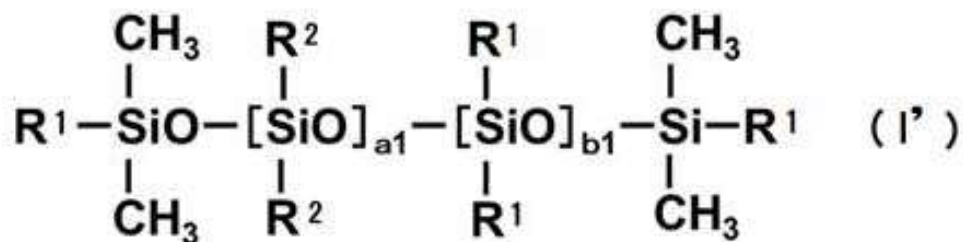
(I), and may be the same or different; and

in the entire general formula (I) including Y¹, when a content of all silicon atoms including terminals is 100 mol%, a content of a₁ is 50 mol% or more and 98 mol% or less, a content of b₁ is 0 mol% or more and 10 mol% or less, a content of c₁ is 0 mol% or more and 30 mol% or less, and a content of d₁ is 0 mol% or more and 50 mol% or less; and in the entire general formula (I) including Y¹, two or more of R¹ are alkenyl groups having 2 or more and 8 or less carbon atoms.

In the general formula (I), when the content of c₁ is 0 mol%, that is, when the alkenyl group-containing silicone does not have a Q unit, examples of the alkenyl group-containing silicone include an organopolysiloxane represented by the following general formula (I').

[0049]

[Formula 6]



[0050]

R² bonded to the silicon atom represented by [SiO]_{a1} may be a monovalent hydrocarbon group containing an alkyl group or an aryl group, but is preferably a monovalent

hydrocarbon group having 1 or more and 16 or less carbon atoms selected from an alkyl group or an aryl group, more preferably a methyl group or a phenyl group, and still more preferably a methyl group.

[0051]

R^1 bonded to the silicon atom represented by $[SiO]_{b1}$ is an alkenyl group having 2 or more and 8 or less carbon atoms, or a monovalent hydrocarbon group containing an alkyl group or an aryl group, and one or more of R^1 may be an alkenyl group having 2 or more and 8 or less carbon atoms, but is preferably an alkenyl group having 2 or more and 8 or less carbon atoms, or a monovalent hydrocarbon group having 1 or more and 16 or less carbon atoms selected from an alkyl group or an aryl group. When R^1 is a hydrocarbon group other than an alkenyl group, a methyl group or a phenyl group is more preferable, and a methyl group is still more preferable.

[0052]

R^1 bonded to the silicon atom represented by $[SiO]_{d1}$ may be an alkenyl group having 2 or more and 8 or less carbon atoms or a monovalent hydrocarbon group containing an alkyl group or an aryl group, but is preferably an alkenyl group having 2 or more and 8 or less carbon atoms or a monovalent hydrocarbon group having 1 or more and 16 or less carbon atoms selected from an alkyl group or an

aryl group, and more preferably a monovalent hydrocarbon group having 1 or more and 16 or less carbon atoms selected from an alkyl group or an aryl group. When R¹ is a hydrocarbon group other than an alkenyl group, a methyl group or a phenyl group is more preferable, and a methyl group is still more preferable.

[0053]

R¹ at each of both terminals of the main chain is also similar to R¹ bonded to the silicon atom represented by [SiO]_{b1}, but an alkenyl group having 2 or more and 8 or less carbon atoms is preferable, and when the alkenyl group at the terminal reacts with an Si-H group, steric structural impediment becomes relatively small, and peelability is easily improved, which is particularly preferable.

[0054]

R¹ bonded to the silicon atom at the terminal in the general formula (Ia) is also similar to R¹ bonded to the silicon atom represented by [SiO]_{b1}, but an alkenyl group having 2 or more and 8 or less carbon atoms is preferable because the cohesive force of the release layer is improved, and the peeling property of a process material through an organic solvent is improved.

[0055]

Examples of the alkenyl group having 2 or more and 8

or less 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.

[0056]

In the entire general formula (I) including Y_1 , when the content of all the silicon atoms including the terminal is 100 mol%, the content of a_1 is 50 mol% or more and 98 mol% or less, but is preferably 70 mol% or more and 98 mol% or less. The content of b_1 is 0 mol% or more and 10 mol% or less, and preferably 0 mol% or more and 5 mol% or less. The content of c_1 is 0.5 mol% or more and 30 mol% or less, and preferably 0.5 mol% or more and 20 mol% or less. The content of d_1 is 0 mol% or more and 50 mol% or less, and preferably 0 mol% or more and 30 mol% or less.

[0057]

When the total content of the constituent units of $[\text{SiO}]_{a_1}$ and $[\text{SiO}]_{b_1}$ is 100 mol%, the content range of the constituent unit of $[\text{SiO}]_{a_1}$ is preferably 90 mol% or more and 100 mol% or less, and more preferably 95 mol% or more and 100 mol% or less, from the viewpoint of localizing the hydrocarbon group on the surface of the coating film in order to improve the peelability.

[0058]

The number average molecular weight of the alkenyl

group-containing silicone is preferably 1,000 or more and less than 10,000, and more preferably 3,000 or more and less than 10,000. When the number average molecular weight is 1,000 or more, the hydrocarbon group is localized on the surface of the coating film and sufficient peelability is easily obtained. Meanwhile, when the number average molecular weight is less than 10,000, the emulsifying property of the alkenyl group-containing silicone in the aqueous coating composition is improved, and the uniform coatability of the aqueous coating composition tends to be also improved.

[0059]

(Si-H group-containing silicone)

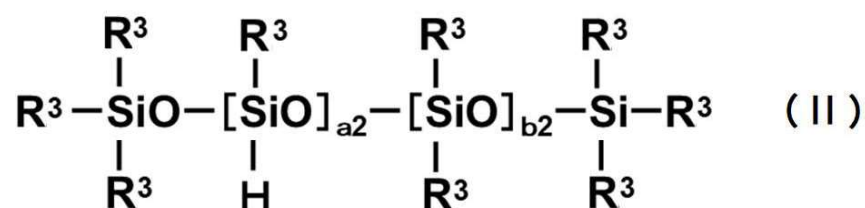
The Si-H group-containing silicone may be any compound as long as the Si-H group-containing silicone is a compound which has two or more Si-H groups (that is, two or more hydrogen atoms directly bonded to an Si atom) in a molecule and has a siloxane bond in a main chain, but a polyorganosiloxane having an Si-H group in a side chain is preferable. A copolymer containing a dialkylsiloxane unit or an alkylphenylsiloxane unit is preferable because it is easy to adjust the amount of Si-H groups in one molecule while exhibiting peelability. A silicon atom at the terminal may have an Si-H group, but preferably has a trialkylsilane structure such as trimethylsilane.

[0060]

Examples of the Si-H group-containing silicone include an organohydrogenpolysiloxane represented by the following general formula (II):

[0061]

[Formula 7]



[0062]

in which R³ is a monovalent hydrocarbon group having 1 or more and 16 or less carbon atoms and containing an alkyl group or an aryl group, which may be the same or different, and when a content of a₂ + b₂ is 100 mol%, a content of a₂ is 30 mol% or more and 90 mol% or less, and a content of b₂ is 10 mol% or more and 70 mol% or less.

A hydrogen atom (hydrogen group) is bonded to the silicon atom represented by [SiO]_{a2}, and R³ may be a monovalent hydrocarbon group containing an alkyl group or an aryl group, but is preferably a monovalent hydrocarbon group having 1 or more and 16 or less carbon atoms selected from an alkyl group or an aryl group.

[0063]

[SiO]_{b2} and R³ bonded to Si atom at the terminal may

be a monovalent hydrocarbon group containing an alkyl group or an aryl group, and is preferably a monovalent hydrocarbon group having 1 or more and 16 or less carbon atoms selected from an alkyl group or an aryl group.

[0064]

For any R^3 , the number of carbon atoms of the alkyl group or the aryl group is more preferably smaller, and steric structural impediment is relatively small, so that the crosslinking reaction easily proceeds. The number of carbon atoms of the alkyl group or the aryl group is also preferably smaller from the viewpoint of fluidity and uniformity of the reaction structure in the release layer. Therefore, the alkyl group is preferably a methyl group, an ethyl group, a propyl group, or a butyl group or the like, and the aryl group is preferably a phenyl group or a tolyl group or the like.

[0065]

When the total content of the constituent units of $[SiO]_{a2}$ and $[SiO]_{b2}$ is 100 mol%, the content range of the constituent unit of $[SiO]_{a2}$ is preferably 30 mol% or more and 90 mol% or less, and more preferably 40 mol% or more and 80 mol% or less. When the content of the structural unit of $[SiO]_{a2}$ is 30 mol% or more, the amount of the crosslinking reaction point is sufficient, the cohesive force of the release layer increases, and the scratch

resistance and solvent resistance of the release layer are also improved, which is preferable. When the content of the constituent unit of $[\text{SiO}]_{\text{a}2}$ is 90 mol% or less, Si-H groups are less likely to remain in the release layer, so that the activity of the surface of the release layer is less likely to increase, and the peelability is favorably maintained, which is preferable.

[0066]

The number average molecular weight of the Si-H group-containing silicone in the present invention is preferably 1,000 or more and 5,000 or less, and more preferably 3,000 or more and 5,000 or less. When the number average molecular weight is 1,000 or more, sufficient peelability is easily obtained. Meanwhile, when the number average molecular weight is 5,000 or less, the emulsification property of the Si-H group-containing silicone in the aqueous coating composition is improved, and the coating uniformity tends to be also improved. In addition, the crosslinking reaction easily proceeds efficiently, the number of remaining Si-H groups in the release layer is reduced, and the peelability is improved.

[0067]

In the aqueous coating composition, the Si-H group-containing silicone is preferably contained in an amount of 1 part by mass or more and 50 parts by mass or less, more

preferably 2 parts by mass or more and 40 parts by mass or less, and still more preferably 3 parts by mass or more and 30 parts by mass or less with respect to 100 parts by mass of the alkenyl group-containing silicone. When the content of the Si-H group-containing silicone is 1 part by mass or more, the crosslinking reaction point becomes a sufficient amount, a dense crosslinked structure is easily formed, and the releasability is improved, which is preferable. The content of the Si-H group-containing silicone is preferably 50 parts by mass or less because the Si-H group in the release layer is less likely to remain, the activity of the surface of the release layer is less likely to increase, and the peelability is favorably maintained.

[0068]

(Polyvinyl alcohol-based resin)

The aqueous coating composition may contain a polyvinyl alcohol-based resin. As such a polyvinyl alcohol-based resin, polyvinyl alcohol, or a copolymer thereof is used. Examples of the polyvinyl alcohol copolymer include a vinyl alcohol-vinyl acetate copolymer, a vinyl alcohol-vinyl butyral copolymer, an ethylene-vinyl alcohol copolymer, and a polyvinyl alcohol-based polymer having a silyl group in a molecule. Among these, a vinyl alcohol-vinyl acetate copolymer and an ethylene-vinyl alcohol copolymer are preferable. When the polyvinyl

alcohol-based resin is a copolymer, the content of the repeating unit derived from vinyl alcohol is preferably 70 mol% or more and 100 mol% or less, and more preferably 85 mol% or more and 99 mol% or less.

[0069]

The polymerization degree of the polyvinyl alcohol-based resin in the present invention can be represented by the viscosity of a 4 mass% aqueous solution at 20°C, and the viscosity is preferably 5 mPa·s or more and 50 mPa·s or less. When the viscosity is within the above-mentioned numerical range, miscibility in the aqueous coating composition is high, and a more uniform release layer is easily obtained. That is, when the viscosity is 5 mPa·s or more, it is difficult to flow in the coating film after the formation of the release layer, and it is difficult to deteriorate the release property, which is preferable. When the viscosity is 50 mPa·s or less, the viscosity of the entire aqueous coating composition is less likely to increase, and uniform coating is facilitated, which is preferable.

[0070]

The polyvinyl alcohol-based resin can also be mixed with silicone before emulsification, and can also be used as an emulsifier.

[0071]

Normally, polyvinyl alcohol is obtained by polymerizing vinyl acetate into polyvinyl acetate and then saponifying the polyvinyl acetate, and the amount of saponification is represented as a degree of saponification. In the present invention, the degree of saponification of the polyvinyl alcohol-based resin is preferably 85 mol% or more and 99 mol% or less. When the degree of saponification is within the above-mentioned numerical range, miscibility in the aqueous coating composition is high, and a more uniform release layer is easily obtained. In particular, when the degree of saponification is 85 mol% or more, the mixing property with silicone is also improved while the adhesion with the substrate is improved. When the degree of saponification is 99% or less, the hydrophilicity of the release layer is not excessively increased, the cohesive force of the release layer coating film is easily maintained, and the adhesion of the release layer is hardly deteriorated.

[0072]

As the polyvinyl alcohol-based resin, a commercially available product can be used as it is. Specific examples of such a commercially available product include Poval manufactured by Kuraray Co., Ltd., Gohsenol manufactured by Mitsubishi Chemical Corporation.

[0073]

When the aqueous coating composition or the release layer in the present invention contains a polyvinyl alcohol-based resin, the polyvinyl alcohol-based resin is preferably contained in an amount of 20% by mass or less based on the release layer. The content is more preferably 1% by mass or more and 15% by mass or less, and still more preferably 1% by mass or more and 10% by mass or less.

When the content of the polyvinyl alcohol-based resin is within the above-mentioned numerical range, it is possible to more suitably achieve two properties, that is, both the mixing property with silicone and adhesion between the substrate and the release layer. That is, when the content of the polyvinyl alcohol-based resin in the release layer is 1% by mass or more, the stability of the silicone emulsion in the coating liquid tends to be improved, and when the content is 20% by mass or less, the release property is less likely to be deteriorated.

[0074]

(Platinum-based catalyst)

The crosslinking reaction between the alkenyl group-containing silicone and the Si-H group-containing silicone is an addition reaction, and in one aspect, a platinum-based catalyst is preferably used for promoting the reaction.

[0075]

Known platinum-based catalysts can be used, and examples thereof include platinum chloride and chloroplatinic acid. In consideration of the dispersibility of the platinum-based catalyst in the silicone, a 1,3-divinyl-1,1,3,3-tetramethyldisiloxane platinum (0) complex (Karstedt catalyst) may be used, and uniform dispersibility can be secured by simultaneously dispersing silicone when emulsifying the silicone.

[0076]

The content of the platinum-based catalyst is preferably set such that the mass of the platinum element is in a range of 10 ppm or more and 400 ppm or less with respect to the total mass of the alkenyl group-containing silicone and the Si-H group-containing silicone. Within such a range, it is possible to sufficiently cure the silicone, to suppress the generation of silicone aggregates, and to obtain a release film excellent in surface property. When the mass ratio of the platinum element is equal to or less than the upper limit, the addition reaction between the alkenyl group and the Si-H group becomes moderate, and the generation of the silicone aggregates tends to be suppressed. From such a viewpoint, the content of the platinum-based catalyst is more preferably 300 ppm or less, and still more preferably 200 ppm or less. When the mass ratio of the platinum element

is equal to or greater than the lower limit, the addition reaction sufficiently proceeds, which hardly causes the poor curing of the silicone. From such a viewpoint, the content of the platinum catalyst is more preferably 15 ppm or more, and still more preferably 20 ppm or more.

[0077]

(Aqueous solvent)

The aqueous coating composition usually contains an aqueous solvent in addition to the alkenyl group-containing silicone and the Si-H group-containing silicone, and as the aqueous solvent, one containing water is preferably used. In one aspect, an aqueous dispersion of an alkenyl group-containing silicone and an aqueous dispersion of an Si-H group-containing silicone are used for the preparation of an aqueous coating composition. As the aqueous dispersion of each silicone, an aqueous emulsion is preferably used.

[0078]

The release layer is formed of such an aqueous emulsion, and the release layer is formed by applying an aqueous coating composition containing the aqueous emulsion (hereinafter, may be abbreviated as "aqueous coating liquid"). By using the aqueous solvent as the aqueous coating liquid, the release layer can be formed without using an explosion-proof facility and a recovery facility required for an organic solvent during the film formation

process. It is also possible to contain some organic solvent as necessary.

[0079]

(Other components)

In one aspect, other additives such as, for example, a surfactant, a coupling agent, a crosslinking reaction inhibitor, an anti-static agent, an ultraviolet absorber, a pigment, a coloring agent, organic or inorganic particles, a lubricant, and an antiblocking agent can be mixed with the aqueous coating composition as long as the effect of the invention is not impaired.

[0080]

(Surfactant)

In one aspect, it is preferable to add a surfactant to the aqueous coating composition in order to promote the wetting of the aqueous coating composition on the substrate film when the release layer is provided. Examples of the surfactant include an anionic surfactant, a cationic surfactant, and a nonionic surfactant, and it is also possible to use one or more of these surfactants. It is preferable to use a nonionic surfactant as the emulsifier in order to prevent the aggregation of the aqueous emulsions of the respective silicones and not to affect the curing reaction of the silicones.

[0081]

The nonionic surfactant preferably has an HLB value of 6 or more and 18 or less, and examples thereof include at least one selected from alkylene oxide adducts such as higher alcohols and 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 the Griffin's calculation formula.

[0082]

Examples of the alkylene oxide include ethylene oxide, propylene oxide, and butylene oxide, and one or two or more of these may be used. When two or more of the alkylene oxides are used, the HLB value is preferably in a range of 8 or more and 18 or less, and more preferably in a range of 10 or more and 15 or less, regardless of a block or random addition form. Among these nonionic surfactants, polyoxyethylene lauryl ether and polyoxyethylene tridecyl ether and the like are preferable. Two or more kinds of nonionic surfactants may be mixed as necessary. When a nonionic surfactant having an HLB value outside such a range is used as an emulsifier of a silicone aqueous dispersion, an emulsification dispersion force and the stability of the aqueous dispersion may be deteriorated.

[0083]

The surfactant is used preferably in a range of 0.1% by mass or more and 20% by mass or less, more preferably in a range of 0.2% by mass or more and 15% by mass or less, and still more preferably in a range of 0.5% by mass or more and 10% by mass or less, with respect to the total solid content. When the content is equal to or greater than the lower limit of this range, the emulsified state becomes good, and when the content is equal to or less than the upper limit of this range, heavy peeling is less likely to occur.

[0084]

(Crosslinking reaction inhibitor)

In one aspect, a reaction inhibitor is preferably contained in order to suppress the activity of the platinum-based catalyst at room temperature in the state of the aqueous coating liquid. Such a reaction inhibitor is preferably a reaction inhibitor having an alkynyl group. The reaction inhibitor having an alkynyl group is not particularly limited as long as the reaction inhibitor has an alkynyl group, and specific examples thereof include 1-ethynyl-1-cyclohexanol, 4-ethyl-1-octyne-3-ol, 3-methyl-1-dodecine-3-ol, 3,7,11-trimethyl-1-dodecine-3-ol, 1,1-diphenyl-2-propyne-3-ol, 3-ethyl-6-ethyl-1-nonine-3-ol, 3-methyl-1-pentadecine-3-ol, 2,5-dimethyl-3-hexine-2,5-diol,

and 3-phenyl-1-butene-3-ol. In the present invention, since the coating liquid is the aqueous coating liquid, it is preferable to use a reaction inhibitor having an alkynyl group and a hydroxyl group as exemplified above from the viewpoint of the balance between affinity solubility in water and coordination ability to platinum, and the boiling point. The platinum-based catalyst may be mixed with a general organopolysiloxane in order to be added to the aqueous coating liquid, and used as an aqueous emulsion.

[0085]

The content of the crosslinking reaction inhibitor is preferably 5 ppm or more and 1,000 ppm or less, more preferably 10 ppm or more and 700 ppm or less, and still more preferably 20 ppm or more and 500 ppm or less, with respect to the mass of the aqueous coating composition to be used for the formation of the release layer. When the content of the crosslinking reaction inhibitor is equal to or greater than the lower limit, the pot life tends to be long, the addition curing reaction of silicone tends to hardly proceed at room temperature, and silicone aggregates tend to be hardly generated. When the content of the crosslinking reaction inhibitor is equal to or less than the upper limit, silicone is less likely to migrate to a mating material after the mating material is peeled off, and the amount of the reaction inhibitor volatilized during

a heat treatment is reduced, so that contamination inside an oven is less likely to occur.

[0086]

(Coupling agent)

In one aspect, a coupling agent can be added to the aqueous coating composition in order to improve adhesion between the silicone component and the substrate film. The coupling agent is, for example, a compound represented by the general formula $YRSiX_3$, and examples thereof include a silane coupling agent. Here, Y is an organic functional group such as a vinyl group, an epoxy group, an amino group, or a mercapto group, and Y is particularly preferably an epoxy group or a vinyl group.

[0087]

R is an alkylene group such as methylene, ethylene, or propylene group, or a single bond. X is a hydrolyzable group such as a methoxy group, an ethoxy group, or acetoxy, or an alkyl group. At least one of three X's is a hydrolyzable group, and three X's are preferably a hydrolyzable group. The hydrolyzable group is preferably a methoxy group.

[0088]

Preferable examples of the silane coupling agent include 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldiethoxysilane, vinyltriethoxysilane,

vinyltriacetoxysilane, vinyltrimethoxysilane, vinyltris(2-methoxyethoxy)silane, and vinylmethyldimethoxysilane.

[0089]

Other examples of the coupling agent include organometallic compounds containing metals such as zirconium, titanium, and aluminum, and the organometallic compounds are preferably those classified into alkoxides, chelates, and acylates. Specific examples thereof include, but are not limited to, zirconium tetraacetylacetonate, zirconium acetate, titanium acetylacetonate, triethanolamine titanate, and titanium lactate.

[0090]

As the coupling agent, it is also possible to use two or more kinds of coupling agents such as combination of a silane coupling agent in which Y is an epoxy group and a silane coupling agent in which Y is a vinyl group.

[0091]

In one aspect, by adding a coupling agent, durable adhesion between silicone as a main component of the release layer and a polyester film or the like is improved. For example, when a resin sheet of a solution casting method using an organic solvent is cast, an organic solvent component may permeate the release layer, and the release layer may be eroded, but the erosion can be suppressed by adding the coupling agent. When the resin sheet is cast by

a melt casting method at a high temperature, the release layer is exposed to a high temperature, which may cause the release layer to be thermally deteriorated. The thermal deterioration of the release layer can be suppressed by adding the coupling agent, and thus the release layer can be held.

[0092]

From the above viewpoint, the content of the coupling agent is preferably 0.1 parts by mass or more and 20 parts by mass or less, and more preferably 1 part by mass or more and 10 parts by mass or less, with respect to a total of 100 parts by mass of the alkenyl group-containing silicone and the Si-H group-containing silicone contained in the release layer.

[0093]

(Preparation of silicone aqueous dispersion)

In one aspect, examples of the preparation of the aqueous emulsion include an emulsifying method using a predetermined alkenyl group-containing silicone or an Si-H group-containing silicone, an aqueous solvent, and a surfactant. A known method can be used for emulsifying these components, and examples thereof include a method in which a predetermined silicone prepared in advance, a surfactant, and other components as necessary are mechanically emulsified in an aqueous medium using a

stirring device such as a homogenizer, an azihomomixer, or an ultra planetary mixer.

[0094]

The particle size of the aqueous dispersion can be adjusted by adjusting the size of a stirring blade, a stirring speed, and a stirring time. The average particle diameter of the dispersed particles of each silicone aqueous dispersion is preferably 200 nm or less, and more preferably 100 nm or more and 200 nm or less.

[0095]

[Substrate film]

The substrate film in the present invention is not particularly limited, and examples thereof include a sheet or a film made of polyesters such as polyethylene terephthalate and polyethylene naphthalate (PEN), polyolefins such as polycarbonate, polyethylene, and polypropylene, polystyrene triacetyl cellulose, acrylic, and polyimide and the like. Among them, a film made of polyester is preferable from the viewpoint of excellent mechanical properties and heat resistance and good balance between these properties and price. Hereinafter, the case of the polyester film will be described as an example, but even when other resin films are used, a copolymerization component, a blend component, an additive, a film production method, and a laminated structure and the like

are the same as those described below.

[0096]

(Polyester film)

Polyester constituting the polyester film to be used as the substrate film is not particularly limited, and film-formed polyester which is generally used as a substrate for a release film can be used. The polyester is preferably crystalline linear saturated polyester composed of an aromatic dibasic acid component and a diol component, and for example, polyethylene terephthalate, polyethylene-2,6-naphthalate, polybutylene terephthalate, polytrimethylene terephthalate, or a copolymer containing constituent components of these resins as main components is more suitable. 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 polymer manufactured from only terephthalic acid and ethylene glycol is preferable. 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.

[0097]

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 0.62 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.

[0098]

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).

[0099]

The method for manufacturing the polyester film of the present invention is not particularly limited, and methods generally used conventionally can be used. For example, the polyester film can be obtained by melting the

polyester with an extruder, extruding the melted product into a film form, cooling the extruded product with a rotary cooling drum to obtain an un-stretched film, and biaxially stretching the un-stretched 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 un-stretched film is simultaneously stretched biaxially in the machine direction and the transverse direction.

[0100]

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 and transverse directions preferably by once or more and 8 times or less and particularly preferably by twice or more and 6 times or less.

[0101]

The thickness of the polyester film is preferably 12 μm or more and 50 μm or less, more preferably 15 μm or more and 38 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. Whereas, the thickness of the film of 50 μm or less is preferable for saving the environmental load, because the amount of the film to be disposed after being used is not extremely large.

[0102]

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.

[0103]

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 having a particle size of 1.0 μm or more, for example, inorganic particles, and therefore the occurrence of defects due to the transfer of the particle shape in the substrate to the resin sheet can be reduced.

[0104]

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 more effectively suppressed.

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 more effectively suppress the occurrence of defects due to the transfer of the particle shape in the substrate to the resin sheet. 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 substantially free of particles having a particle size of 1.0 μm or more.

[0105]

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 actively contained.

[0106]

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.

[0107]

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.

[0108]

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 5,000 ppm or more and 15,000 ppm or less in total.

[0109]

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 5 nm or more and 35 nm or less. When the total content of the silica particles and/or the calcium carbonate particles is 5,000 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 15,000 ppm or less and the S_a is 40 nm or less, the aggregation of the lubricant is less likely to occur, and coarse protrusions cannot be formed, so that the quality is stable during the manufacture of the ultrathin

ceramic green sheet, which is preferable.

[0110]

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.

[0111]

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 0.5 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.

[0112]

From the viewpoint of reducing pinholes, it is preferable not to use a recycled raw material or the like for the surface layer A, which is a layer on which the release layer is to be provided, in order to prevent the contamination of inorganic particles such as a lubricant.

[0113]

The thickness ratio of the surface layer A, which is a layer on which the release layer is to be provided, is preferably 20% or more and 50% or less of the total thickness of all the layers of the substrate film. When the thickness ratio of the surface layer A is 20% or more, the film is hardly affected from the inside of the film by particles contained in the surface layer B or the like, and the average area surface roughness S_a easily satisfies the above range, which is preferable. When the thickness ratio of the surface layer A is 50% or less of the total thickness of all the layers of the substrate film, the use ratio of a recycled raw material in the surface layer B can be increased, so that the environmental load is reduced,

which is preferable.

[0114]

From the viewpoint of economic performance, for the layer other than the surface layer A (the surface layer B or the above-mentioned intermediate layer C), 50% by mass or more and 90% by mass or less of film scraps or reused materials for PET bottles can be used. Even in this case, it is preferable that the type, the amount, and the particle size of the lubricant contained in the layer B, and the average area surface roughness (Sa) of the surface layer B satisfy the above ranges.

[0115]

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 surface treatment or the like.

[0116]

In one aspect, the release layer-formed surface to which the aqueous coating composition is applied can be subjected to a surface treatment or provided with an easily adhesive layer in order to enhance adhesion to the release

layer. Examples of the surface treatment include a plasma treatment, a corona discharge treatment, an ultraviolet treatment, a flame treatment, and an electron beam/radiation treatment, and examples of the easily adhesive layer include a layer containing the same resin as that of the substrate film, and further containing an anti-static agent, a pigment, a surfactant, a lubricant, and an anti-blocking agent and the like. When an adhesion improver such as a coupling agent is added to the aqueous coating composition, the release layer can have sufficient adhesion to the substrate film without providing an easily adhesive layer or the like.

[0117]

[Formation of release layer]

In one aspect, the release layer is formed by applying an aqueous coating composition containing an aqueous emulsion of an alkenyl group-containing silicone and an aqueous emulsion of an Si-H group-containing silicone. At this time, the release layer is formed on at least one surface of the substrate film. The release layer is formed by applying the aqueous coating liquid onto the substrate film, then heating and drying, and reacting and solidifying components of the aqueous coating liquid. The release layer is preferably formed in a film forming step.

[0118]

The thickness of the release layer is preferably 5 nm or more and 100 nm or less as the thickness after drying. When the thickness of the release layer is equal to or greater than the lower limit, the peelability is easily sufficiently obtained, and when the thickness is equal to or less than the upper limit, the peeling strength tends not to increase, and there is no need to increase the concentration of the release layer component of the aqueous coating liquid or increase the coating amount, so that coating tends to be easy. Therefore, the thickness of the release layer is more preferably 5 nm or more and 70 nm or less, and still more preferably 5 nm or more and 50 nm or less.

[0119]

When the aqueous coating liquid is applied onto the substrate film, the solid content concentration thereof is preferably 20% by mass or less, and more preferably 1% by mass or more and 10% by mass or less, based on the release layer component in the aqueous coating liquid. When the solid content concentration of the release layer component in the aqueous coating liquid is equal to or greater than the lower limit, the film formability tends to be improved. When the solid content concentration is equal to or less than the upper limit, the stability of the aqueous coating liquid and the appearance of the release layer tend to be

improved. Water is preferably used as the aqueous solvent for adjusting the solid concentration.

[0120]

The aqueous coating liquid applied to the substrate film to form the release layer can be carried out at any stage, but is preferably carried out in the process of manufacturing the polyester film, and is preferably applied to the polyester film before the orientation crystallization is completed. Thereafter, the film is stretched in at least one direction, and then heat-treated to allow the crystal orientation to be completed.

[0121]

Here, the polyester film before the completion of the crystal orientation includes an unstretched film, a uniaxially oriented film obtained by orienting the unstretched film in either a machine direction (hereinafter, may be referred to as a film continuous film formation direction, a machine direction, or an MD direction) or a transverse direction (hereinafter, may be referred to as a direction orthogonal to the machine direction, a width direction, or a TD direction), and a film obtained by subjecting the unstretched film to stretching and orientation at a low magnification in two directions of 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 the orientation crystallization).

[0122]

Among them, so-called in-line coating is preferable, in which an aqueous coating liquid is applied to an unstretched film or a uniaxially stretched film oriented in one direction, and machine stretching and/or transverse stretching and heat fixation are performed as they are. The release layer may be dried by a stretching step or a heat fixation treatment after application, 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 can be cured by a stretching step or a heat fixation treatment, but a curing step may be further added as necessary.

[0123]

When the aqueous coating liquid is applied to the polyester film, it is preferable to subject the surface of the film 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 together with the composition as a wetting agent in combination, or to additionally add a surfactant as the wetting agent.

[0124]

As a coating 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, and a curtain coating method and the like can be used alone or in combination.

[0125]

[Characteristics of release film]

In the present invention, the release layer preferably has surface free energy in a range of 10 mN/m or more and 40 mN/m or less, more preferably 12 mN/m or more and 38 mN/m or less, still more preferably 14 mN/m or more and 36 mN/m or less, and particularly preferably 15 mN/m or more and 35 mN/m or less in a test method described later. When the surface free energy of the release layer is equal to or less than the upper limit, the adhesion force is reduced, and heavy peeling hardly occurs. When the surface free energy is equal to or greater than the lower limit, defects due to cissing of a processed layer such as a ceramic sheet or a resin sheet applied to the surface of the release layer hardly occur, and pinhole defects also hardly occur.

[0126]

[Application]

The release film in the present invention can be used as a process film used during manufacturing of a multilayer ceramic capacitor, or casting of a resin sheet, or the like. In particular, even when a thin film resin sheet having a thickness of 1 μm or less after drying is prepared, the wettability is good, so that the pinholes of the processed layer are reduced, and for example, when the thin film resin sheet is used for a release film for manufacturing a green sheet, the defect rate of a thin multilayer ceramic capacitor can be reduced.

EXAMPLES

[0127]

Hereinafter, the present invention will be more specifically described with reference to Examples and Comparative Examples, but the present invention is not limited to the following Examples. The evaluation methods of physical properties and the like in the following Examples are as follows.

[0128]

(1) Coating uniformity of release layer

A release film was cut into A4 size, and the number of cohesive application defects (the number per A4 size) was compared when the surface of a release layer was visually observed using a fluorescent lamp and a halogen

light, and evaluated according to the following criteria.

⊙: No application defects

○: 1 to 2 application defects

△: 3 to 5 application defects

×: 6 or more application defects

[0129]

(2) Surface free energy of release layer

Under the conditions of 23°C and 50%RH, a sample subjected to humidity control for 24 hours was measured for a static contact angle when water was added dropwise and the sample was allowed to stand for 30 seconds using a contact angle meter (DMo-501 manufactured by Kyowa Interface Science Co., Ltd.). Similarly, the static contact angles of ethylene glycol and methylene iodide were measured, and the following simultaneous equations regarding the surface tension component of the release layer were set using the surface tension components of the following liquids (the respective measurement liquids of water, ethylene glycol, and methylene iodide are 1, 2, and 3, γ_{LD} represents a dispersion force component of the liquid, γ_{LP} represents a polar force component of the liquid, γ_{LH} represents a hydrogen bond component of the liquid, γ_L represents a total value of the respective surface tension components in the liquid, γ_{SD} represents a dispersion force component of the release layer, γ_{SP}

represents a polar force component of the release layer, and γ_{SH} represents a hydrogen bond component of the release layer. θ represents a contact angle).

$$(\gamma_{SD} \cdot \gamma_{LD1})^{1/2} + (\gamma_{SP} \cdot \gamma_{LP1})^{1/2} + (\gamma_{SH} \cdot \gamma_{LH1})^{1/2} = \gamma_{L1}(1 + \cos\theta_1)/2$$

$$(\gamma_{SD} \cdot \gamma_{LD2})^{1/2} + (\gamma_{SP} \cdot \gamma_{LP2})^{1/2} + (\gamma_{SH} \cdot \gamma_{LH2})^{1/2} = \gamma_{L2}(1 + \cos\theta_2)/2$$

$$(\gamma_{SD} \cdot \gamma_{LD3})^{1/2} + (\gamma_{SP} \cdot \gamma_{LP3})^{1/2} + (\gamma_{SH} \cdot \gamma_{LH3})^{1/2} = \gamma_{L3}(1 + \cos\theta_3)/2$$

γ_{LD} , γ_{LP} , γ_{LH} , and γ_L of water, ethylene glycol, and methylene iodide are as shown in Table 1.

[0130]

[Table 1]

	Dispersion force	Polar force	Hydrogen bond	Total
	γ_{LD}	γ_{LP}	γ_{LH}	γ_L
Water	29.1	1.3	42.4	72.8
Ethylene glycol	30.1	0.0	17.6	47.7
Methylene iodide	46.8	4.0	0.0	50.8

[0131]

Next, from the numerical values of γ_{SD} , γ_{SP} , and γ_{SH} obtained above, the surface free energy γ_S of the surface of the release layer was calculated using the following formula.

$$\gamma_S = \gamma_{SD} + \gamma_{SP} + \gamma_{SH}$$

[0132]

(3) Smear test of release layer (friction resistance)

The release surface of the release film was rubbed once with an index finger under a load of about 500 gf, and the whitened state of the surface of the release layer was visually observed and evaluated according to the following criteria.

○: No change

△: Slight whitening

×: Whitening

[0133]

(4) Rub-off value of release layer (adhesion)

The release surface of the release film was rubbed with a thumb at a load of about 500 gf 10 times, and an adhesive tape (trade name "31B Tape" manufactured by Nitto Denko Corporation) was bonded thereto in order to confirm silicone falling off at the portion, and the peeling state of the adhesive tape was confirmed and evaluated according to the following criteria.

○: No peeling change when adhesive tape is peeled off

△: Slight peeling change when adhesive tape is peeled off

×: Peeling change when adhesive tape is peeled off

[0134]

(5) Peelability of ceramic sheet

100 parts by mass of barium titanate (BaTiO_3)

manufactured by KCM Corporation), 7 parts by mass of polyvinyl butyral (manufactured by Sekisui Chemical Co., Ltd.), 3 parts by mass of dioctyl phthalate, and 3 parts by mass of a dispersant (DISPERBYK-103 manufactured by BYK-Chemie) were added to a mixed solvent of toluene : ethanol = 1 : 1 (volume ratio), and dispersed by a ball mill to prepare a slurry. This slurry was uniformly applied onto the release layer of the release film so that the thickness after drying was 2 μm , and then dried to form a ceramic sheet. The release film on which the ceramic sheet was formed was cut into 25 mm $\times$ 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. This test piece was subjected to humidity control for 24 hours under conditions of 23°C and a humidity of 50%, and then the ceramic sheet was peeled off at a peeling angle of 180° and a peeling rate of 300 mm/min using a tensile tester to measure the peeling strength. For the peeling strength of the ceramic sheet, superiority and inferiority were determined from the following indexes.

⊙: Peeling strength is less than 1 g/25 mm

○: Peeling strength is 1 g/25 mm or more and less than 3 g/25 mm

△: Peeling strength is 3 g/25 mm or more and 12 g/25

mm or less

×: Peeling strength is more than 12 g/25 mm, or the ceramic sheet is broken.

[0135]

(6) Evaluation of recyclability

For the recyclability, the size and number of foreign matters contained in the film were enlarged 20 times by down irradiation with a universal projector, and the number of foreign matters having a maximum diameter of 50 μm or more was counted. The measurement area was 0.05 m^2 .

⊙: The number of foreign matters is less than 10 foreign matters/0.05 m^2 , which does not cause a problem in use.

○: The number of foreign matters is 10 foreign matters/0.05 m^2 or more and less than 30 foreign matters/0.05 m^2 , which slightly affects the flatness but does not cause a problem in use.

△: The number of foreign matters is 30 foreign matters/0.05 m^2 or more and less than 100 foreign matters/0.05 m^2 , which can be used with limited applications.

×: The number of foreign matters is 100 foreign matters/0.05 m^2 or more, which makes the deformation of the cast surface significantly noticeable, and cannot be used.

[0136]

(7) Number average molecular weight

Gel permeation chromatography (GPC) was measured and calculated in terms of polystyrene.

[0137]

(8) Thickness of release layer

The release film was cut into triangular small pieces, and then a Pt (platinum) layer having a thickness of 2 nm was formed on the surface of the release layer by coating. The obtained sample was fixed in a multi-axis embedding capsule, embedded using an epoxy resin, and sliced in a direction perpendicular to the plane direction of the film using a microtome ULTRACUT-S to obtain an ultrathin sample having a thickness of 50 nm. Next, the obtained ultrathin sample was mounted on a grid, and was steam-stained with 2% osmium acid at 60°C for 2 hours. Using the steam-stained ultrathin sample, the cross section of the film was observed with a transmission electron microscope LEM-2000 under the condition of an acceleration voltage of 100 kV, and the thickness of the release layer was measured. The measurement was performed at 10 arbitrary points, and the average value thereof was taken as the thickness (unit: nm) of the release layer.

[0138]

[Example 1-1]

Polyethylene terephthalate ($[\eta] = 0.64$ dl/g, $T_g =$

78°C) containing 0.1% by mass of calcium carbonate particles having an average particle size of 0.6 µm was melted by an extruder, passed through a filter having a filtration accuracy of 10 µm, extruded from a die, and cooled by a cooling drum by a conventional method to obtain an unstretched film. Subsequently, the film was stretched 3.3 times at 80°C in a machine direction, and then an aqueous coating liquid (aqueous coating composition) obtained in Manufacturing Example 1-1 was uniformly applied with a roll coater so that a release layer had a thickness shown in Table 2 in terms of product thickness. The aqueous coating liquid used was within 24 hours after preparation.

[0139]

Next, the film after application was dried at 110°C, stretched 4.5 times in a transverse direction at 140°C, and heat-fixed at 235°C for about 10 seconds to obtain a release film (thickness: 25 µm) having a release layer formed by reacting and solidifying the aqueous coating liquid, and the release film was evaluated. The evaluation results are shown in Table 2.

[0140]

A release film portion that did not become a product at the time of collecting a product roll, and a release film that did not become a product due to defects and the

like were pulverized until a film piece major diameter became about 5 mm or less for each of Examples and Comparative Examples, and melted. 40% by mass of the regenerated raw material was used.

[0141]

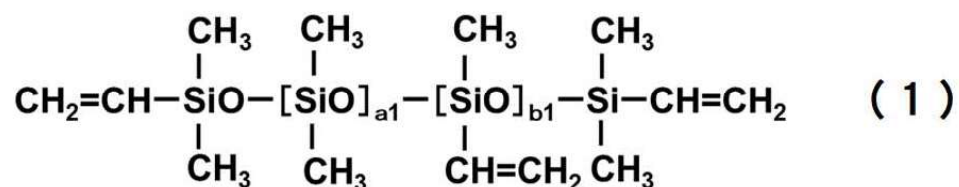
<Manufacturing Example 1-1>

(Sample 1-1A)

An aqueous emulsion of Sample 1-1A having a solid content of 50% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 96% by mass of a silicone oil in which a1 in formula (1) was 100 mol%, b1 was 0 mol%, and the number average molecular weight was 9,000, and 4% by mass of polyoxyethylene tridecyl ether (trade name "LEOCOL TD-90" manufactured by Lion Specialty Chemicals Co., Ltd.) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 210 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0142]

[Formula 8]



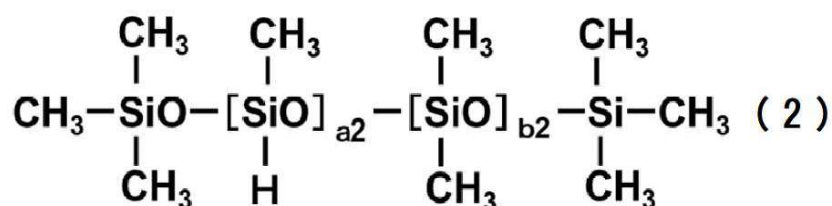
[0143]

(Sample 1-2A)

An aqueous dispersion of Sample 1-2A having a solid content of 50% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 96% by mass of a silicone oil in which a2 in formula (2) was 50 mol%, b2 was 50 mol%, and the number average molecular weight was 3,000, and 4% by mass of polyoxyethylene tridecyl ether (trade name "LEOCOL TD-90" manufactured by Lion Specialty Chemicals Co., Ltd.) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 170 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0144]

[Formula 9]



[0145]

(Aqueous coating liquid)

An aqueous coating liquid was prepared so that the solid content mass of the silicone of Sample 1-1A and Sample 1-2A was a blending amount shown in Table 2, and the other components were as follows. 3% by mass of the following coupling agent with respect to the total mass of silicone, 60 ppm of the following platinum-based catalyst with respect to the total mass of the solid content of Sample 1-1 and Sample 1-2, and 120 ppm of the following crosslinking reaction inhibitor with respect to the mass of the aqueous coating liquid were mixed, and the solid concentration of the aqueous coating liquid was diluted with water so as to have a target release layer thickness, thereby preparing an aqueous coating liquid.

- Coupling agent: 3-glycidoxypropyltriethoxysilane (trade name "Sila-Ace S510" manufactured by JNC Corporation)

- Platinum-based catalyst: platinum-based catalyst emulsion (trade name "CATALYST EM440" manufactured by Wacker, inc.)

- Crosslinking reaction inhibitor: 1-ethynylcyclohexanol (manufactured by Alfa Lancaster)

[0146]

[Examples 1-2 and 1-3]

Release films were prepared under exactly the same conditions as in Example 1-1 except that the contents of Sample 1-1A and Sample 1-2A were changed as shown in Table 2 when the aqueous coating liquid was prepared in Example 1-1, and evaluated as described above. The results are shown in Table 2.

[0147]

[Example 1-4]

A release film was produced under exactly the same conditions as in Example 1-1 except that the aqueous coating liquid was prepared using Sample 1-1B manufactured in Manufacturing Example 1-2 in place of Sample 1-1A in Example 1-1, and evaluated as described above. The results are shown in Table 2.

[0148]

<Manufacturing Example 1-2>

(Sample 1-1B)

An aqueous emulsion of Sample 1-1B having a solid content of 50% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 96% by mass of a silicone oil in which a1 in formula (1) was 100 mol%, b1 was 0 mol%, and the number average molecular weight was 5,000, and 4% by mass of polyoxyethylene tridecyl ether (trade name "LEOCOL TD-90" manufactured by Lion Specialty Chemicals Co., Ltd.) as a

surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 190 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0149]

[Example 1-5]

A release film was produced under exactly the same conditions as in Example 1-1 except that the aqueous coating liquid was prepared using Sample 1-1C manufactured in manufacturing Example 1-3 in place of Sample 1-1A in Example 1-1, and evaluated as described above. The results are shown in Table 2.

[0150]

<Manufacturing Example 1-3>

(Sample 1-1C)

An aqueous emulsion of Sample 1-1C having a solid content of 50% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 96% by mass of a silicone oil in which a1 in formula (1) was 100 mol%, b1 was 0 mol%, and the number average molecular weight was 3,000, and 4% by mass of polyoxyethylene tridecyl ether (trade name "LEOCOL TD-90" manufactured by Lion Specialty Chemicals Co., Ltd.) as a

surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 170 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0151]

[Example 1-6]

A release film was produced under exactly the same conditions as in Example 1-1 except that the aqueous coating liquid was prepared using Sample 1-1D manufactured in manufacturing Example 1-4 in place of Sample 1-1A in Example 1-1, and evaluated as described above. The results are shown in Table 2.

[0152]

<Manufacturing Example 1-4>

(Sample 1-1D)

An aqueous emulsion of Sample 1-1D having a solid content of 50% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 96% by mass of a silicone oil in which a1 in formula (1) was 96 mol%, b1 was 4 mol%, and the number average molecular weight was 7,000, and 4% by mass of polyoxyethylene tridecyl ether (trade name "LEOCOL TD-90" manufactured by Lion Specialty Chemicals Co., Ltd.) as a

surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 200 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0153]

[Comparative Examples 1-1 to 1-3]

Release films were prepared under exactly the same conditions as in Examples 1-1 to 1-3 except that the aqueous coating liquid obtained in Manufacturing Example 1-5 was used in place of the aqueous coating liquid obtained in Manufacturing Example 1-1 in Examples 1-1 to 1-3, and evaluated as described above. The results are shown in Table 2.

[0154]

[Manufacturing Example 1-5]

(Sample 1-1E)

An aqueous emulsion of Sample 1-1E having a solid content of 50% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 96% by mass of a silicone oil in which a1 in formula (1) was 97 mol%, b1 was 3 mol%, and the number average molecular weight was 30,000, and 4% by mass of polyoxyethylene tridecyl ether (trade name "LEOCOL TD-90"

manufactured by Lion Specialty Chemicals Co., Ltd.) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 200 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0155]

(Sample 1-2B)

An aqueous dispersion of Sample 1-2B having a solid content of 50% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 96% by mass of a silicone oil in which a₂ in formula (2) was 55 mol%, b₂ was 45 mol%, and the number average molecular weight was 7,000, and 4% by mass of polyoxyethylene tridecyl ether (trade name "LEOCOL TD-90" manufactured by Lion Specialty Chemicals Co., Ltd.) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 190 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0156]

(Aqueous coating liquid)

An aqueous coating liquid was prepared under the same conditions as in Manufacturing Example 1-1 except that the aqueous coating liquid was prepared so that the solid content mass of the silicone of Sample 1-1E and Sample 1-2B was a blending amount shown in Table 2.

[0157]

[Comparative Example 1-4]

A substrate film was produced in the same manner as in Example 1-1 except that the release layer was not applied in Example 1-1. In terms of solid content ratio, 88% by mass of silicone in which a1 in formula (1) was 96 mol%, b1 was 4 mol%, and the number average molecular weight was 150,000, 9% by mass of silicone in which a2 in formula (2) was 80 mol%, b2 was 20 mol%, and the number average molecular weight was 20,000, and 3% by mass of a catalyst: CM670 (manufactured by Momentive Performance Materials Inc.) were mixed, a necessary amount of a platinum-based catalyst was added to the mixture, and the solid content concentration of the coating liquid was diluted with an organic solvent containing 70% by mass of methyl ethyl ketone and 30% by mass of toluene so as to have a target release layer thickness, thereby preparing a coating liquid. The coating liquid was applied to the substrate film using a coating machine to form a release layer, and drying was performed at a temperature of 130°C

for 30 seconds to prepare a release film, and the release film was evaluated as described above. The results are shown in Table 2. Since the release layer was formed using the organic solvent, a special explosion-proof facility was required, and the exhaust treatment of the dried organic solvent was also unnecessarily required as compared with Examples.

[0158]

[Comparative Example 1-5]

A substrate film was produced in the same manner as in Example 1-1 except that the release layer was not applied. In terms of solid content ratio, 88% by mass of silicone in which a1 in formula (1) was 99 mol%, b1 was 1 mol%, and the number average molecular weight was 8,000, 9% by mass of silicone in which a2 in formula (2) was 60 mol%, b2 was 40 mol%, and the number average molecular weight was 4,000, and 3% by mass of a catalyst: CM670 (manufactured by Momentive Performance Materials Inc.) were mixed, and the solid content concentration of the coating liquid was diluted with an organic solvent containing 70% by mass of methyl ethyl ketone and 30% by mass of toluene so as to have a target release layer thickness, thereby preparing a coating liquid. The coating liquid was applied to the substrate film using a coating machine to form a release layer, and drying was performed at a temperature of 130°C

for 30 seconds to prepare a release film, and the release film was evaluated as described above. The results are shown in Table 2. Since the release layer was formed using the organic solvent, a special explosion-proof facility was required, and the exhaust treatment of the dried organic solvent was also unnecessarily required as compared with Examples.

[0159]

[Table 2]

Item		Unit	Example 1-1	Example 1-2	Example 1-3	Example 1-4	Example 1-5	Example 1-6
Release layer	Sample 1-1A (Mn = 9000)	% by mass	90	80	70			
	Sample 1-1B (Mn = 5000)					90		
	Sample 1-1C (Mn = 3000)						90	
	Sample 1-1D (Mn = 7000)							90
	Sample 1-1E (Mn = 30000)							
	Sample 1-2A (Mn = 3000)		10	20	30	10	10	10
	Sample 1-2B (Mn = 7000)							
	Thickness	μm	0.03	0.03	0.03	0.03	0.03	0.03
Evaluation	Coating uniformity		⊙	⊙	⊙	⊙	⊙	⊙
	Surface free energy	mN/m	16	16	16	16	17	17
	Smear (friction resistance)		○	○	○	○	○	○
	Rub-off (adhesion)		○	○	○	○	○	○
	Peelability of ceramic sheet		○	⊙	○	⊙	⊙	○
	Recyclability		⊙	⊙	○	⊙	⊙	○
	Comprehensive evaluation		⊙	⊙	○	⊙	⊙	○

Item		Unit	Comparative Example 1-1	Comparative Example 1-2	Comparative Example 1-3	Comparative Example 1-4	Comparative Example 1-5
Release layer	Sample 1-1A (Mn = 9000)	% by mass				-	-
	Sample 1-1B (Mn = 5000)					-	-
	Sample 1-1C (Mn = 3000)					-	-
	Sample 1-1D (Mn = 7000)					-	-
	Sample 1-1E (Mn = 30000)		90	80	70	-	-
	Sample 1-2A (Mn = 3000)					-	-
	Sample 1-2B (Mn = 7000)		10	20	30	-	-
	Thickness	μm	0.03	0.03	0.03	0.10	0.10
Evaluation	Coating uniformity		○	△	×	○	○
	Surface free energy	mN/m	15	15	15	15	16
	Smear (friction resistance)		○	○	○	○	○
	Rub-off (adhesion)		○	○	○	△	△
	Peelability of ceramic sheet		○	○	△	△	△
	Recyclability		△	△	×	×	○
	Comprehensive evaluation		△	△	×	×	△

[0160]

As shown in Table 2, in Examples 1-1 to 1-6, it was easy to achieve both the peelability and wettability of the release layer, and a release film including the release layer having good coating uniformity and recyclability was obtained. Meanwhile, in Comparative Examples 1-1 to 1-3 in which the molecular weight of silicone was large, coating uniformity tended to be deteriorated, the ceramic sheet tended to cause heavy peeling, and the recyclability also deteriorated. In Comparative Examples 1-4 to 1-5 in which the release layer was formed offline using a solvent-type coating liquid, the coating uniformity of the release layer and the adhesion of the release layer were deteriorated, and particularly in Comparative Example 1-4 in which the molecular weight of silicone was large, the recyclability was also deteriorated.

[0161]

[Example 2-1]

Polyethylene terephthalate ($[\eta] = 0.65 \text{ dl/g}$, $T_g = 78^\circ\text{C}$) containing 0.15% by mass of calcium carbonate particles having an average particle size of $0.6 \mu\text{m}$ was melted by an extruder, passed through a filter having a filtration accuracy of $10 \mu\text{m}$, extruded from a die, and cooled by a cooling drum by a conventional method to obtain an unstretched film. Subsequently, the film was stretched

3.2 times at 80°C in a machine direction, and then an aqueous coating liquid (aqueous coating composition) obtained in Manufacturing Example 2-1 was uniformly applied with a roll coater so that a release layer had a thickness shown in Table 3 in terms of product thickness. The aqueous coating liquid used was within 24 hours after preparation.

[0162]

Next, the film after application was dried at 105°C, stretched 4.6 times in a transverse direction at 145°C, and heat-fixed at 230°C for about 10 seconds to obtain a release film (thickness: 25 µm) having a release layer formed by reacting and solidifying the aqueous coating liquid, and the release film was evaluated. The evaluation results are shown in Table 3.

[0163]

A release film portion that did not become a product at the time of collecting a product roll, and a release film that did not become a product due to defects and the like were pulverized until a film piece major diameter became about 5 mm or less for each of Examples and Comparative Examples, and melted. 45% by mass of the regenerated raw material was used.

[0164]

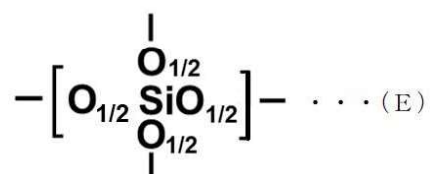
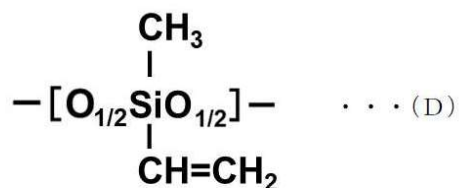
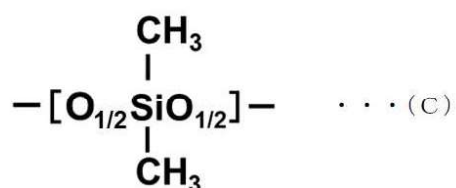
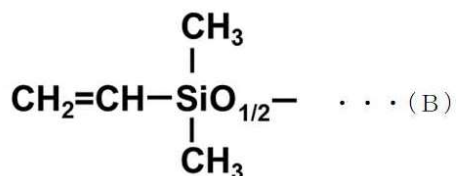
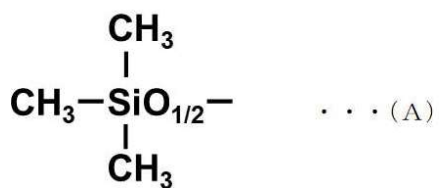
[Manufacturing Example 2-1]

(Sample 2-1A)

An aqueous emulsion of Sample 2-1A having a solid content of 45% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 95% by mass of a silicone oil represented by formula (A) as 2 mol%, formula (B) as 4 mol%, formula (C) as 90 mol%, formula (D) as 2 mol%, and formula (E) as 2 mol%, and having a number average molecular weight of 8,000 and 5% by mass of polyoxyethylene tridecyl ether (trade name "Adekato1 TN-100" manufactured by ADEKA CORPORATION) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 200 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0165]

[Formula 10]



[0166]

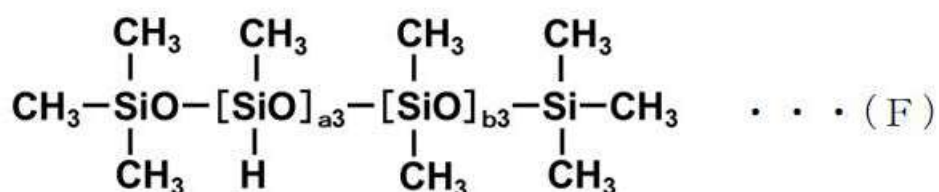
(Sample 2-2A)

An aqueous dispersion of Sample 2-2A having a solid content of 40% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 95% by mass of a silicone oil in which a3 in formula (F) was 60 mol%, b3 was 40 mol%, and the number average molecular weight was 4,000, and 5% by mass of polyoxyethylene tridecyl ether (trade name "Adekato1 TN-

100" manufactured by ADEKA CORPORATION) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 180 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0167]

[Formula 11]



[0168]

(Aqueous coating liquid)

An aqueous coating liquid was prepared so that the solid content mass of the silicone of Sample 2-1A and Sample 2-2A was a blending amount shown in Table 3, and the other components were as follows. 5% by mass of the following coupling agent with respect to the total mass of silicone, 50 ppm of the following platinum-based catalyst with respect to the total mass of the solid content of Sample 2-1A and Sample 2-2A, and 100 ppm of the following crosslinking reaction inhibitor with respect to the mass of the aqueous coating liquid were mixed, and the solid

concentration of the aqueous coating liquid was diluted with water so as to have a target release layer thickness, thereby preparing the aqueous coating liquid.

- Coupling agent: 3-glycidoxypentyltriethoxysilane (trade name "KBE-403" manufactured by Shin-Etsu Chemical Co., Ltd.)

- Platinum-based catalyst: platinum-based catalyst emulsion (trade name "CATALYST EM440" manufactured by Wacker, inc.)

- Crosslinking reaction inhibitor: 1-ethynylcyclohexanol (manufactured by Alfa Lancaster)

[0169]

[Examples 2-2 and 2-3]

A release film was prepared under exactly the same conditions as in Example 2-1 except that the contents of Sample 2-1A and Sample 2-2A were changed as shown in Table 3 when the aqueous coating liquid was prepared in Example 2-1, and evaluated as described above. The results are shown in Table 3.

[0170]

[Example 2-4]

A release film was produced under exactly the same conditions as in Example 2-2 except that the aqueous coating liquid was prepared using Sample 2-1B manufactured in Manufacturing Example 2-2 in place of Sample 2-1A in

Example 2-2, and evaluated as described above. The results are shown in Table 3.

[0171]

<Manufacturing Example 2-2>

(Sample 2-1B)

An aqueous emulsion of Sample 2-1B having a solid content of 50% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 95% by mass of a silicone oil represented by formula (A) as 3 mol%, formula (B) as 7 mol%, formula (C) as 85 mol%, formula (D) as 2 mol%, and formula (E) as 3 mol%, and having a number average molecular weight of 4,000 and 5% by mass of polyoxyethylene tridecyl ether (trade name "Adekato1 TN-100" manufactured by ADEKA CORPORATION) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 180 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0172]

[Example 2-5]

A release film was produced under exactly the same conditions as in Example 2-2 except that the aqueous coating liquid was prepared using Sample 2-1C manufactured

in Manufacturing Example 2-3 in place of Sample 2-1A in Example 2-2, and evaluated as described above. The results are shown in Table 3.

[0173]

<Manufacturing Example 2-3>

(Sample 2-1C)

An aqueous emulsion of Sample 2-1C having a solid content of 40% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 95% by mass of a silicone oil represented by formula (A) as 10 mol%, formula (B) as 5 mol%, formula (C) as 84 mol%, formula (D) as 1 mol%, and formula (E) as 10 mol%, and having a number average molecular weight of 6,000 and 5% by mass of polyoxyethylene tridecyl ether (trade name "Adekato1 TN-100" manufactured by ADEKA CORPORATION) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 210 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0174]

[Comparative Examples 2-1 to 2-3]

A release film was prepared under exactly the same conditions as in Examples 2-1 to 2-3 except that the

aqueous coating liquid obtained in Manufacturing Example 2-4 was used in place of the aqueous coating liquid obtained in Manufacturing Example 2-1 in Examples 2-1 to 2-3, and evaluated as described above. The results are shown in Table 3.

[0175]

<Manufacturing Example 2-4>

(Sample 2-1D)

An aqueous emulsion of Sample 2-1D having a solid content of 40% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 95% by mass of a silicone oil represented by formula (A) as 30 mol%, formula (B) as 5 mol%, formula (C) as 30 mol%, formula (D) as 1 mol%, and formula (E) as 34 mol%, and having a number average molecular weight of 250,000 and 5% by mass of polyoxyethylene tridecyl ether (trade name "Adekamol TN-100" manufactured by ADEKA CORPORATION) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 300 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0176]

(Sample 2-2B)

An aqueous dispersion of Sample 2-2B having a solid content of 50% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 95% by mass of a silicone oil in which a₃ in formula (F) was 50 mol%, b₃ was 50 mol%, and the number average molecular weight was 8,000, and 5% by mass of polyoxyethylene tridecyl ether (trade name "Adekato1 TN-100" manufactured by ADEKA CORPORATION) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 210 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0177]

(Aqueous coating liquid)

An aqueous coating liquid was prepared under the same conditions as in manufacturing Example 2-1 except that the aqueous coating liquid was prepared so that the solid content mass of the silicone of Sample 2-1D and Sample 2-2B was a blending amount shown in Table 3.

[0178]

[Comparative Example 2-4]

A substrate film was produced in the same manner as in Example 2-1 except that the release layer was not

applied. A coating liquid was prepared by mixing 80% by mass of silicone: SD-7335 (addition reaction type, number average molecular weight 900,000, manufactured by Dow Toray Co., Ltd.), 20% by mass silicone: SD-7236 (addition reaction type containing silicone resin, number average molecular weight 580,000, manufactured by Dow Toray Industries, Inc.), and 0.02% by mass of a catalyst: SRX-212 (manufactured by Dow Toray Industries, Inc.) in terms of solid content ratio, and diluting the solid content concentration of the coating liquid with toluene so as to have a target release layer thickness. The coating liquid was applied to the substrate film using a coating machine to form a release layer, and drying was performed at a temperature of 150°C for 30 seconds to prepare a release film, and the release film was evaluated as described above. The results are shown in Table 3. Since the release layer was formed using the organic solvent, a special explosion-proof facility was required, and the exhaust treatment of the dried organic solvent was also unnecessarily required as compared with Examples.

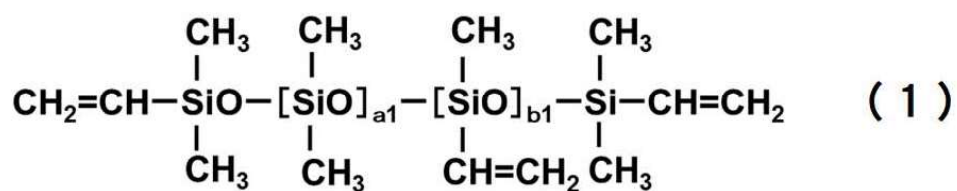
[Comparative Example 2-5]

A substrate film was produced in the same manner as in Example 2-1 except that the release layer was not applied. In terms of solid content ratio, 88% by mass of silicone in which a1 in formula (1) was 96 mol%, b1 was 4

mol%, and the number average molecular weight was 150,000, 9% by mass of silicone in which a2 in formula (2) was 80 mol%, b2 was 20 mol%, and the number average molecular weight was 20,000, and 3% by mass of a catalyst: CM670 (manufactured by Momentive Performance Materials Inc.) were mixed, a necessary amount of a platinum-based catalyst was added to the mixture, and the solid content concentration of the coating liquid was diluted with an organic solvent containing 70% by mass of methyl ethyl ketone and 30% by mass of toluene so as to have a target release layer thickness, thereby preparing a coating liquid. The coating liquid was applied to the substrate film using a coating machine to form a release layer, and drying was performed at a temperature of 130°C for 30 seconds to prepare a release film, and the release film was evaluated as described above. The results are shown in Table 3. Since the release layer was formed using the organic solvent, a special explosion-proof facility was required, and the exhaust treatment of the dried organic solvent was also unnecessarily required as compared with Examples.

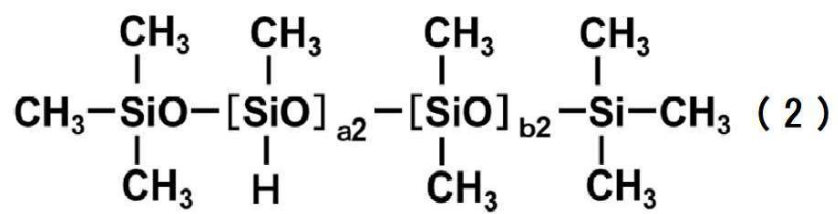
[0179]

[Formula 12]



[0180]

[Formula 13]



[0181]

[Table 3]

Item		Q unit	Unit	Example 2-1	Example 2-2	Example 2-3	Example 2-4	Example 2-5
Release layer	Sample 2-1A (Mn = 8000)	2 mol%	% by mass	95	90	85		
	Sample 2-1B (Mn = 4000)	3 mol%					90	
	Sample 2-1C (Mn = 6000)	10 mol%						90
	Sample 2-1D (Mn = 250000)	34 mol%						
	Sample 2-2A (Mn = 4000)	-		5	10	15	10	10
	Sample 2-2B (Mn = 8000)	-						
	Thickness		μm	0.03	0.03	0.03	0.03	0.03
Evaluation	Coating uniformity			⊙	⊙	○	⊙	○
	Surface free energy		mN/m	20	20	19	21	21
	Smear (friction resistance)			○	○	○	○	○
	Rub-off (adhesion)			○	○	○	○	○
	Peelability of ceramic sheet			⊙	⊙	○	⊙	⊙
	Recyclability			⊙	⊙	○	⊙	⊙
	Comprehensive evaluation			⊙	⊙	○	⊙	⊙

Item		Q unit	Unit	Comparative Example 2-1	Comparative Example 2-2	Comparative Example 2-3	Comparative Example 2-4	Comparative Example 2-5
Release layer	Sample 2-1A (Mn = 8000)	2 mol%	% by mass				-	-
	Sample 2-1B (Mn = 4000)	3 mol%					-	-
	Sample 2-1C (Mn = 6000)	10 mol%					-	-
	Sample 2-1D (Mn = 250000)	34 mol%		95	90	85	-	-
	Sample 2-2A (Mn = 4000)	-					-	-
	Sample 2-2B (Mn = 8000)	-		5	10	15	-	-
	Thickness		μm	0.03	0.03	0.03	0.20	0.10
Evaluation	Coating uniformity			△	△	×	○	○
	Surface free energy		mN/m	21	21	20	18	15
	Smear (friction resistance)			△	△	○	○	○
	Rub-off (adhesion)			○	○	○	○	△
	Peelability of ceramic sheet			○	○	△	○	△
	Recyclability			△	×	×	×	×
	Comprehensive evaluation			△	×	×	×	×

[0182]

As shown in Table 3, in Examples 2-1 to 2-5, it was easy to achieve both the peelability and wettability of the release layer, and a release film including the release layer having good coating uniformity and recyclability was obtained. Meanwhile, in Comparative Examples 2-1 to 2-3 in which the molecular weight of silicone was large, coating uniformity tended to be deteriorated, the ceramic sheet tended to cause heavy peeling, and the recyclability also deteriorated. In Comparative Examples 2-4 and 2-5 in which the release layer was formed offline using a solvent-type coating liquid, and the silicone having a large molecular weight was used, the recyclability was deteriorated. In particular, in Comparative Example 2-5, the adhesion of the release layer was reduced, which made it difficult to achieve both the peelability and wettability of the release layer.

[0183]

[Example 3-1]

Polyethylene terephthalate ($[\eta] = 0.63 \text{ dl/g}$, $T_g = 78^\circ\text{C}$) containing 0.25% by mass of calcium carbonate particles having an average particle size of $0.6 \mu\text{m}$ was melted by an extruder, passed through a filter having a filtration accuracy of $10 \mu\text{m}$, extruded from a die, and cooled by a cooling drum by a conventional method to obtain

an unstretched film. Subsequently, the film was stretched 3.2 times at 80°C in a machine direction, and then an aqueous coating liquid (aqueous coating composition) obtained in Manufacturing Example 3-1 was uniformly applied with a roll coater so that a release layer had a thickness shown in Table 4 in terms of product thickness. The aqueous coating liquid used was within 24 hours after preparation.

[0184]

Next, the film after application was dried at 105°C, stretched 4.6 times in a transverse direction at 145°C, and heat-fixed at 230°C for about 10 seconds to obtain a release film (thickness: 25 µm) having a release layer formed by reacting and solidifying the aqueous coating liquid, and the release film was evaluated. The evaluation results are shown in Table 4.

[0185]

A release film portion that did not become a product at the time of collecting a product roll, and a release film that did not become a product due to defects and the like were pulverized until a film piece major diameter became about 5 mm or less for each of Examples and Comparative Examples, and melted. 40% by mass of the regenerated raw material was used.

[0186]

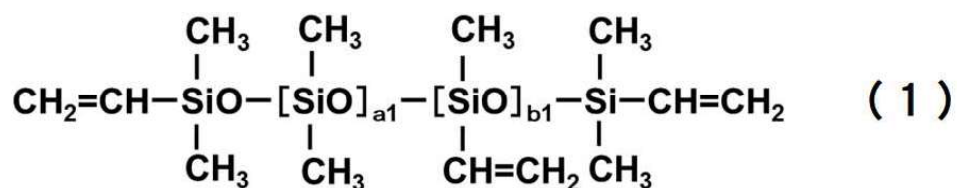
<Manufacturing Example 3-1>

(Sample 3-1A)

An aqueous dispersion of Sample 3-1A having a solid content of 40% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 97% by mass of a silicone oil in which a1 in formula (1) was 100 mol%, b1 was 0 mol%, and the number average molecular weight was 8,000, and 3% by mass of polyoxyethylene tridecyl ether (trade name "EMULGEN 1108" manufactured by Kao Corporation) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 200 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0187]

[Formula 14]



[0188]

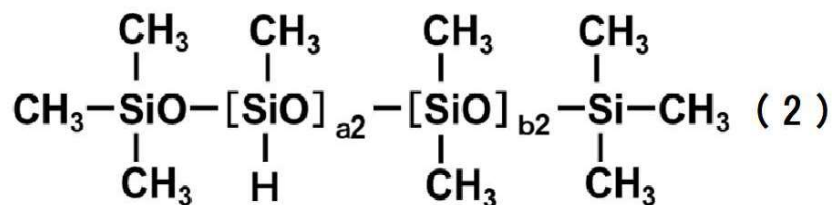
(Sample 3-2A)

An aqueous dispersion of Sample 3-2A having a solid content of 40% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed

of 96% by mass of a silicone oil in which a₂ in formula (2) was 50 mol%, b₂ was 50 mol%, and the number average molecular weight was 3500, and 4% by mass of polyoxyethylene tridecyl ether (trade name "EMULGEN 1108" manufactured by Kao Corporation) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 180 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0189]

[Formula 15]



[0190]

(Aqueous coating liquid)

An aqueous coating liquid was prepared so that the solid content mass of the silicone of Sample 3-1A and Sample 3-2A was a blending amount shown in Table 4, and the other components were as follows. 5% by mass of the following polyvinyl alcohol and 3% by mass of the following coupling agent with respect to the total mass of silicone, 50 ppm of the following platinum-based catalyst with

respect to the total mass of the solid content of Sample 3-1A and Sample 3-2A, and 100 ppm of the following crosslinking reaction inhibitor with respect to the mass of the aqueous coating liquid were mixed, and the solid concentration of the aqueous coating liquid was diluted with water so as to have a target release layer thickness, thereby preparing the aqueous coating liquid.

- Polyvinyl alcohol: polyvinyl alcohol having a viscosity of 27 mPa·s (an aqueous solution having a concentration of 4% by mass, temperature 20°C) and a degree of saponification of 96 mol% (trade name "Kuraray Poval 27-96" manufactured by Kuraray Co., Ltd.)

- Coupling agent: 3-glycidoxypropyltriethoxysilane (trade name "KBE-403" manufactured by Shin-Etsu Chemical Co., Ltd.)

- Platinum-based catalyst: platinum-based catalyst emulsion (trade name "CATALYST EM440" manufactured by Wacker, inc.)

- Crosslinking reaction inhibitor: 1-ethynylcyclohexanol (manufactured by Alfa Lancaster)

[0191]

[Example 3-2]

A release film was produced under exactly the same conditions as in Example 3-1 except that the aqueous coating liquid was prepared using Sample 3-1B manufactured

in Manufacturing Example 3-2 in place of Sample 3-1A in Example 3-1, and evaluated as described above. The results are shown in Table 4.

<Manufacturing Example 3-2>

(Sample 3-1B)

An aqueous dispersion of Sample 3-1B having a solid content of 40% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 97% by mass of a silicone oil in which a1 in formula (1) was 100 mol%, b1 was 0 mol%, and the number average molecular weight was 4,000, and 3% by mass of polyoxyethylene tridecyl ether (trade name "EMULGEN 1108" manufactured by Kao Corporation) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 180 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0192]

[Example 3-3]

A release film was produced under exactly the same conditions as in Example 3-1 except that the aqueous coating liquid was prepared using Sample 3-1C manufactured in Manufacturing Example 3-3 in place of Sample 3-1A in Example 3-1, and evaluated as described above. The results

are shown in Table 4.

[0193]

<Manufacturing Example 3-3>

(Sample 3-1C)

An aqueous dispersion of Sample 3-1C having a solid content of 40% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 97% by mass of a silicone oil in which a1 in formula (1) was 98 mol%, b1 was 2 mol%, and the number average molecular weight was 8,000, and 3% by mass of polyoxyethylene tridecyl ether (trade name "EMULGEN 1108" manufactured by Kao Corporation) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 200 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0194]

[Examples 3-4]

A release film was produced under exactly the same conditions as in Example 3-1 except that the aqueous coating liquid was prepared using Sample 3-1D manufactured in Manufacturing Example 3-4 in place of Sample 3-1A in Example 3-1, and evaluated as described above. The results are shown in Table 4.

[0195]

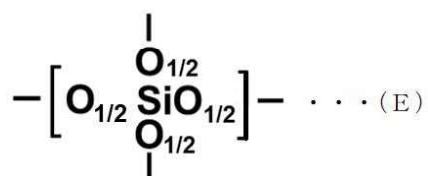
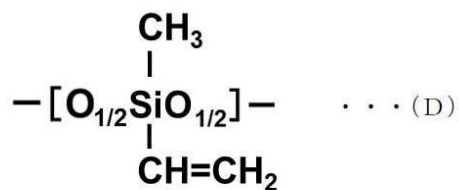
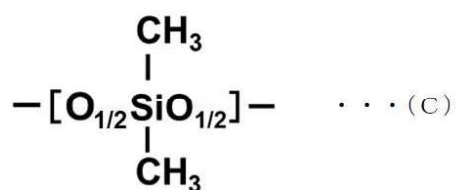
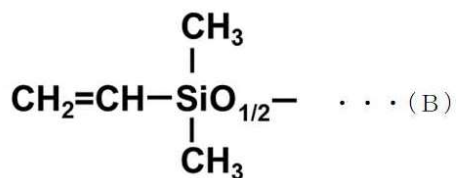
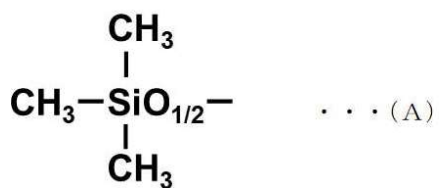
<Manufacturing Example 3-4>

(Sample 3-1D)

An aqueous emulsion of Sample 3-1D having a solid content of 40% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 97% by mass of a silicone oil represented by formula (A) as 1 mol%, formula (B) as 3 mol%, formula (C) as 93 mol%, formula (D) as 2 mol%, and formula (E) as 1 mol%, and having a number average molecular weight of 7,000 and 3% by mass of polyoxyethylene tridecyl ether (trade name "EMULGEN 1108" manufactured by Kao Corporation) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 180 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0196]

[Formula 16]



[0197]

[Example 3-5]

A release film was prepared under exactly the same conditions as in Example 3-4 except that the contents of Sample 3-1D and Sample 3-2A were changed as shown in Table 4 when the aqueous coating liquid was prepared in Example 3-4, and evaluated as described above. The results are shown in Table 4.

[0198]

[Example 3-6]

A release film was produced under exactly the same conditions as in Example 3-1 except that the aqueous coating liquid was prepared using Sample 3-1E manufactured in Manufacturing Example 3-5 in place of Sample 3-1A in Example 3-1, and evaluated as described above. The results are shown in Table 4.

[0199]

<Manufacturing Example 3-5>

(Sample 3-1E)

An aqueous emulsion of Sample 3-1E having a solid content of 40% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 97% by mass of a silicone oil represented by formula (A) as 2 mol%, formula (B) as 4 mol%, formula (C) as 91 mol%, formula (D) as 1 mol%, and formula (E) as 2 mol%, and having a number average molecular weight of 3,000 and 3% by mass of polyoxyethylene tridecyl ether (trade name "EMULGEN 1108" manufactured by Kao Corporation) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 170 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0200]

[Examples 3-7]

A release film was prepared under exactly the same conditions as in Example 3-1 except that the aqueous coating liquid was prepared using the following polyvinyl alcohol in place of polyvinyl alcohol (trade name "Kuraray Poval 27-96" manufactured by Kuraray Co., Ltd.) in Example 3-1, and evaluated as described above. The results are shown in Table 4.

· Polyvinyl alcohol: polyvinyl alcohol having a viscosity of 23 mPa·s (an aqueous solution having a concentration of 4% by mass, temperature 20°C) and a degree of saponification of 88 mol% (trade name "Gohsenol GM-14R" manufactured by Mitsubishi Chemical Corporation)

[0201]

[Comparative Examples 3-1 and 3-2]

A release film was prepared under exactly the same conditions as in Examples 3-4 and 3-5 except that the aqueous coating liquid obtained in Manufacturing Example 3-6 was used in place of the aqueous coating liquid obtained in Manufacturing Example 3-4 in Examples 3-4 and 3-5, and evaluated as described above. The results are shown in Table 4.

[0202]

<Manufacturing Example 3-6>

(Sample 3-1F)

An aqueous emulsion of Sample 3-1F having a solid content of 40% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 96% by mass of a silicone oil represented by formula (A) as 35 mol%, formula (B) as 5 mol%, formula (C) as 25 mol%, formula (D) as 2 mol%, and formula (E) as 33 mol%, and having a number average molecular weight of 270,000 and 4% by mass of polyoxyethylene tridecyl ether (trade name "EMULGEN 1108" manufactured by Kao Corporation) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 260 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0203]

(Sample 3-2B)

An aqueous dispersion of Sample 3-2B having a solid content of 50% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 96% by mass of a silicone oil in which a₂ in formula (2) was 50 mol%, b₂ was 50 mol%, and the number average molecular weight was 9,000, and 4% by mass of polyoxyethylene tridecyl ether (trade name "EMULGEN 1108"

manufactured by Kao Corporation) as a surfactant using an emulsifier (manufactured by N. P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. An emulsion particle size was adjusted to an average particle size of 230 nm by adjusting a stirring speed and a stirring time at the time of emulsification.

[0204]

(Aqueous coating liquid)

An aqueous coating liquid was prepared under the same conditions as in Manufacturing Example 3-1 except that the aqueous coating liquid was prepared so that the solid content mass of the silicone of Sample 3-1F and Sample 3-2B was a blending amount shown in Table 4.

[0205]

[Reference Example 3-3]

A release film was prepared under exactly the same conditions as in Example 3-4 except that polyvinyl alcohol was not added as another component of the release layer in Example 3-4, and evaluated as described above. The results are shown in Table 4.

[0206]

[Comparative Example 3-4]

A substrate film was produced in the same manner as in Example 3-1 except that the release layer was not applied. 86.9% by mass of silicone: KS-774 (manufactured

by Shin-Etsu Astec Co., Ltd., addition reaction type, number average molecular weight 750,000), 13% by mass of silicone: KS-3800 (resin type, manufactured by Shin-Etsu Astec Co., Ltd.), and 0.1% by mass of a catalyst: CAT-PL-50T (manufactured by Shin-Etsu Chemical Co., Ltd.) were mixed in terms of solid content ratio, and the solid content concentration of a coating liquid was diluted with toluene so as to have a target release layer thickness, thereby preparing the coating liquid. The coating liquid was applied to the substrate film using a coating machine to form a release layer, and drying was performed at a temperature of 150°C for 30 seconds to prepare a release film, and the release film was evaluated as described above. The results are shown in Table 4. Since the release layer was formed using an organic solvent, coating in a special explosion-proof facility was required, and the exhaust treatment of the dried organic solvent was also unnecessarily required as compared with Examples.

[0207]

[Comparative Example 3-5]

In order to form a primer layer instead of the release layer, a coating liquid described later was applied to prepare a substrate film formed in the same manner as in Example 3-1. As the coating liquid in place of the release layer, 70% by mass of polyvinyl alcohol: Gohsenol GL-03

(manufactured by Mitsubishi Chemical Corporation), 25% by mass of a polyester resin: Plascoat Z-561 (manufactured by GOO CHEMICAL CO., LTD.), and 5% by mass of a surfactant: EMULGEN 420 (manufactured by Kao Corporation) were mixed in terms of solid content ratio, and the solid content concentration of the coating liquid was adjusted with water so that the coating thickness after film formation was 30 nm.

[0208]

A release layer was coated on the surface of the primer layer of the substrate film on which the coating film was formed in the same manner as in Comparative Example 3-4. The results are shown in Table 4. Since the release layer was formed using an organic solvent as in Comparative Example 3-4, coating in a special explosion-proof facility was required, and the exhaust treatment of the dried organic solvent was also unnecessarily required as compared with Examples.

[0209]

[Table 4]

Item		Q unit	Unit	Example 3-1	Example 3-2	Example 3-3	Example 3-4	Example 3-5	Example 3-6	Example 3-7
Release layer	Sample 3-1A (Mn=8000)	0 mol%	% by mass	92						92
	Sample 3-1B (Mn=4000)	0 mol%			92					
	Sample 3-1C (Mn=8000)	0 mol%				92				
	Sample 3-1D (Mn=7000)	1 mol%					92	80		
	Sample 3-1E (Mn=3000)	2 mol%							92	
	Sample 3-1F (Mn=270000)	33 mol%								
	Sample 3-2A (Mn=3500)	-		8	8	8	8	20	8	8
	Sample 3-2B (Mn=9000)	-								
	Polyvinyl alcohol		Presence or absence	Presence	Presence	Presence	Presence	Presence	Presence	Presence
	Thickness		μm	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Primer layer			Presence or absence	Absence	Absence	Absence	Absence	Absence	Absence	Absence
Evaluation	Coating uniformity			⊙	⊙	⊙	⊙	⊙	⊙	⊙
	Surface free energy		mN/m	22	23	24	24	24	25	21
	Peelability of ceramic sheet			○	○	○	⊙	⊙	⊙	○
	Smear (friction resistance)			○	○	○	○	○	○	○
	Rub-off (adhesion)			○	○	○	○	○	○	○
	Recyclability			⊙	⊙	○	⊙	⊙	⊙	⊙
	Comprehensive evaluation			○	○	○	⊙	⊙	⊙	○

Item		Q unit	Unit	Comparative Example 3-1	Comparative Example 3-2	Reference Example 3-3	Comparative Example 3-4	Comparative Example 3-5
Release layer	Sample 3-1A (Mn=8000)	0 mol%	% by mass				-	-
	Sample 3-1B (Mn=4000)	0 mol%					-	-
	Sample 3-1C (Mn=8000)	0 mol%						
	Sample 3-1D (Mn=7000)	1 mol%				92		
	Sample 3-1E (Mn=3000)	2 mol%						
	Sample 3-1F (Mn=270000)	33 mol%		92	80			
	Sample 3-2A (Mn=3500)	-				8	-	-
	Sample 3-2B (Mn=9000)	-		8	20		-	-
	Polyvinyl alcohol		Presence or absence	Presence	Presence	Absence	-	-
	Thickness		μm	0.02	0.02	0.02	0.10	0.10
Primer layer			Presence or absence	Absence	Absence	Absence	Absence	Presence
Evaluation	Coating uniformity			Δ	Δ	○	⊙	⊙
	Surface free energy		mN/m	24	24	20	19	18
	Peelability of ceramic sheet			○	○	○	Δ	○
	Smear (friction resistance)			○	○	○	○	○
	Rub-off (adhesion)			○	○	Δ	Δ	○
	Recyclability			Δ	×	○	×	×
	Comprehensive evaluation			Δ	×	Δ	×	×

[0210]

As shown in Table 4, in Examples 3-1 to 3-7, it was easy to achieve both the peelability and wettability of the release layer, and the release film including the release layer having good coating uniformity and recyclability was obtained. Meanwhile, in Comparative Examples 3-1 and 3-2 in which the molecular weight of silicone was large, coating uniformity tended to be deteriorated, the ceramic sheet tended to cause heavy peeling, and the recyclability also deteriorated. In Reference Example 3-3 in which the release layer was formed using the aqueous coating liquid containing no polyvinyl alcohol, the adhesion of the release layer was slightly reduced.

[0211]

In Comparative Examples 3-4 and 3-5 in which the release layer was formed offline using the solvent-based coating liquid and the silicone having a large molecular weight was used, the wettability was deteriorated and the recyclability was deteriorated. In particular, in Comparative Example 3-4, the adhesion of the release layer was also deteriorated.

INDUSTRIAL APPLICABILITY

[0212]

The release film of the present invention has high

coating uniformity and peelability of the release layer, has relatively good wettability, is easy to use as a film for various processes, has recyclability, can reduce the load on the environment, and has an extremely high industrial utility value.

CLAIMS

1. A release film comprising:
a substrate film; and
a release layer formed by reacting and solidifying an aqueous coating composition,

wherein the aqueous coating composition contains
an alkenyl group-containing silicone which has two or more alkenyl groups in a molecule, may have a Q unit represented by $\text{SiO}_{4/2}$, and has a number average molecular weight of 1000 or more and less than 10,000, and

an Si-H group-containing silicone having two or more Si-H groups in a molecule and having a number average molecular weight of 1,000 or more and 5,000 or less.

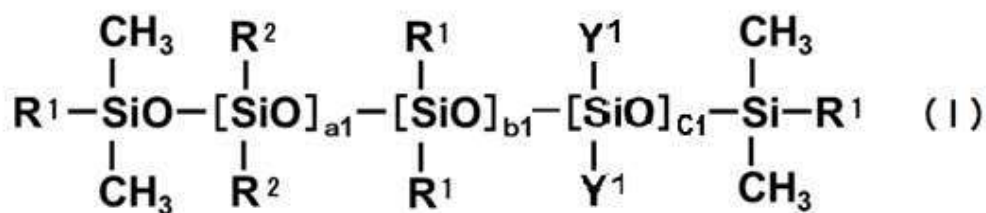
2. The release film according to claim 1, wherein the aqueous coating composition contains a polyvinyl alcohol-based resin.

3. The release film according to claim 2, wherein the polyvinyl alcohol-based resin has a viscosity of 5 mPa·s or more and 50 mPa·s or less, when an aqueous solution having a concentration of 4% by mass is measured at a temperature of 20°C, and has a degree of saponification of 85 mol% or more and 99 mol% or less.

4. The release film according to claim 1, wherein the alkenyl group-containing silicone has a Q unit represented by $\text{SiO}_{4/2}$.

5. The release film according to claim 1, wherein the alkenyl group-containing silicone is represented by the following general formula (I):

[Formula 1]



wherein R^1 is an alkenyl group having 2 or more and 8 or less carbon atoms or a monovalent hydrocarbon group having 1 or more and 16 or less carbon atoms and containing an alkyl group or an aryl group, which may be the same or different;

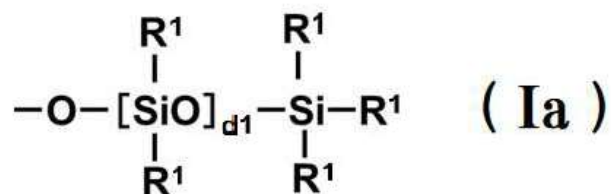
one or more of R^1 bonded to a silicon atom represented by $[\text{SiO}]_{b1}$ are an alkenyl group having 2 or more and 8 or less carbon atoms;

R^2 is a monovalent hydrocarbon group having 1 or more and 16 or less carbon atoms and containing an alkyl group or an aryl group, which may be the same or different;

Y^1 is represented by the general formula (Ia) which

may be the same or different;

[Formula 2]



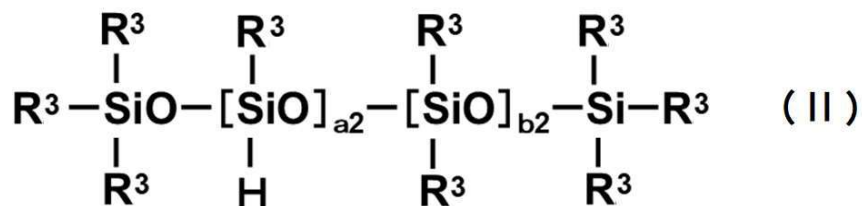
wherein R¹ is the same as R¹ in the general formula (I), and may be the same or different;

in the entire general formula (I) including Y¹, when a content of all silicon atoms including terminals is 100 mol%, a content of a1 is 50 mol% or more and 98 mol% or less, a content of b1 is 0 mol% or more and 10 mol% or less, a content of c1 is 0 mol% or more and 30 mol% or less, and a content of d1 is 0 mol% or more and 50 mol% or less; and

in the entire general formula (I) including Y¹, two or more of R¹ are alkenyl groups having 2 or more and 8 or less carbon atoms.

6. The release film according to claim 1, wherein the Si-H group-containing silicone is represented by the following general formula (II):

[Formula 3]



wherein R³ is a monovalent hydrocarbon group having 1 or more and 16 or less carbon atoms and containing an alkyl group or an aryl group, which may be the same or different; and

when a content of a₂ + b₂ is 100 mol%, a content of a₂ is 30 mol% or more and 90 mol% or less, and a content of b₂ is 10 mol% or more and 70 mol% or less.

7. The release film according to claim 1, wherein the aqueous coating composition contains 1 part by mass or more and 50 parts by mass or less of the Si-H group-containing silicone with respect to 100 parts by mass of the alkenyl group-containing silicone.

8. The release film according to claim 1, wherein the release layer is formed by applying the aqueous coating composition to the substrate film before completion of crystal orientation, stretching the substrate film in at least one direction, and then subjecting the substrate film to a heat treatment to complete the crystal orientation.

9. The release film according to claim 1, wherein the substrate film is a polyester film.

10. The release film according to any one of claims 1 to 9, wherein the release film is a release film for a multilayer ceramic capacitor or a release film for a resin sheet.