Organopolysiloxane composition for the formation of cured release films
Organopolysiloxan-Zusammensetzung für härtbare Trennschichten
Composition d’organopolysiloxane pour former des revêtements reticulés anti-adhésifs

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US-A-4 562 096
EP-A-0 491 598

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The present invention relates to an organopolysiloxane composition for the formation of cured release films (hereinafter referred to as a release film-forming organopolysiloxane composition).

Release film-forming organopolysiloxane compositions based on higher alkyl (typically hexyl)-containing organopolysiloxanes are already known. Because these compositions cure rapidly at relatively low temperatures not exceeding 100°C to yield cured films that are highly releaseable with respect to tacky materials, such release film-forming organopolysiloxane compositions are useful for such applications as release paper, separation or anti-blocking paper. See those compositions disclosed in Japanese Application [Kokai] No. 2-145549 and Japanese Application [Kokai] No. 2-145560. However, compositions of this type are poorly adherent for various types of substrates, such as paper, synthetic films, and polyethylene-laminated kraft paper. As a result the cured films of such compositions readily delaminate from these substrates.

A composition whose crosslinking component comprises an organohydrogenpolysiloxane that contains at least 1 alkyl group and at least 2 silicon-bonded hydrogen atoms in each molecule is disclosed in Japanese Application [Kokai] No. 3-356079. In contrast, the present invention is a composition that uses a special crosslinking component which cures even faster and is more substrate-adherent.

The present invention relates to a release film-forming organopolysiloxane composition which comprises: (A) 100 weight parts of an organopolysiloxane that contains in each molecule at least 2 alkyl group of general formula H₂C=CH₂-(CH₂)ₘ wherein m has a value of from 2 to 8; (B) 1 to 200 weight parts of an octyl-containing organohydrogenpolysiloxane having at least two silicon-bonded hydrogen atoms; (C) an addition-reaction inhibitor; and (D) a catalytic quantity of a platinum-group metal catalyst. Optionally, the composition can further comprise (E) 1 to 200 weight parts of a nonreactive organopolysiloxane.

The present invention introduces a release film-forming organopolysiloxane composition which cures rapidly at relatively low temperatures not exceeding 100°C to afford a cured film that is highly adherent for various types of substrates and that is also highly releasing for tacky or sticky materials.

The organopolysiloxane comprising component (A) contains at least 2 alkyl groups of general formula H₂C=CH₂-(CH₂)ₘ in each molecule. In the preceding formula, m has a value of from 2 to 8 and preferably a value of 3 to 8. When m falls below 2, the composition of the instant invention will have a slow rate of cured film formation. On the other hand, it is difficult to synthesize this type of organopolysiloxane in which m exceeds 8. No specific restriction attaches to the degree of polymerization (DP) of this organopolysiloxane, and an organopolysiloxane can be used which ranges from a low-DP organopolysiloxane with a viscosity of 100 mPa's (centipoise) at 25°C up to a high-DP organopolysiloxane gum. The organopolysiloxane under consideration is exemplified by an organopolysiloxane having the following average unit formula RₜSiOₜ/ₐ-b/₂. In the preceding formula, R is a substituted or unsubstituted monovalent hydrocarbon group and is exemplified by alkyl groups such as methyl, ethyl, propyl, and butyl; alkyl groups such as butyl, pentenyl, hexenyl, and heptenyl; aryl groups such as phenyl, tolyl, and xylyl; and substituted alkyl groups such as 2-phenylethyl, 2-phenylpropyl, and 3,3,3-trifluoropropyl. Methyl preferably comprises at least 70 mol% of R from the perspective of release properties, and b is a number with a value of 1.9 to 2.05. Furthermore, this organopolysiloxane may contain small quantities of silicon-bonded hydroxy or alkox groups.

Component (A) is exemplified by dimethylbutenylsiloxyl-terminated dimethylpolysiloxanes; dimethylpentenylsiloxyl-terminated dimethylpolysiloxanes; dimethylhexenylsiloxyl-terminated dimethylpolysiloxanes; dimethylheptenylsiloxyl-terminated dimethylpolysiloxanes; ethylmethyldecenyloxy-terminated dimethylpolysiloxanes; trimethylsiloxyl-terminated butenylmethylsiloxane-dimethylsiloxane copolymers; silanediyl-terminated butenylmethylsiloxane-dimethylsiloxane copolymers; trimethylsiloxyl-terminated butenylmethylsiloxane-dimethylsiloxane copolymers; trimethylsiloxyl-terminated pentenylsiloxane-dimethylsiloxane copolymers; trimethylsiloxyl-terminated butenylmethylsiloxane-dimethylsiloxane copolymers; trimethylsiloxyl-terminated hexenylmethylsiloxane-dimethylsiloxane copolymers; trimethylsiloxyl-terminated heptenylsiloxane-dimethylsiloxane copolymers; trimethylsiloxyl-terminated octenylsiloxane-dimethylsiloxane copolymers; trimethylsiloxyl-terminated methylpentenylsiloxane-dimethylsiloxane copolymers; dimethylhexenylsiloxyl-terminated hexenylmethylsiloxane-dimethylsiloxane copolymers; and dimethylhexenylsiloxyl-terminated dihexenylmethylsiloxane-dimethylsiloxane copolymers.

Component (B) of the present invention is a crosslinker for component (A) and comprises an organohydrogenpolysiloxane that contains at least 2 silicon-bonded hydrogen atoms and at least 1 octyl group in each molecule. Component (B) also functions to provide the composition of the present invention with adherence for the surface of various types of substrates. In the preceding formula, n is to have a value of 4 to 10 for the following reasons: the improvement in adherence is inadequate at values below 4, while the synthesis of this component becomes problematic at values in excess of 10. It is preferred for purposes of the present invention that n have a value of 8. Furthermore, the alkyl group is preferably present at 2 to 50 mol% in each molecule.

Component (B) is exemplified by octyl-containing organohydrogenpolysiloxanes, such as trimethylsiloxyl-terminated methylpentenylsiloxane-dimethylsiloxane-hydrogenmethylsiloxane copolymers; trimethylsiloxyl-terminated hydrogen-
methylsiloxane-octylhydrogensiloxane copolymers, trimethylsiloxy-terminated dimethylsiloxane-octylhydrogensiloxane copolymers, trimethylsiloxy-terminated methyloctylsiloxane-hydrogenmethylsiloxane copolymers. Component (B) is added at 1 to 200 weight parts per 100 weight parts component (A).

Component (C) of the present invention is essential for equipping the composition of the present invention with storage stability at room temperature. This component is specifically but nonexhaustively exemplified by alkyne alcohols, such as 3-methyl-1-butyn-3-ol, 3,5-dimethyl-1-hexyn-3-ol, and phenylbutynol; ene-yne compounds such as 3-methyl-3-pentene-1-yne and 3,5-dimethyl-3-hexene-1-yne, and by tetramethyltetrahexayclocetotetrasiloxane, or benzotriaazole. This component can be added in a quantity that provides a practically useful pot life. Because the reaction-inhibiting effect varies with the molecular structure of this component, the use quantity is not specifically restricted and the addition should be selected as desired. However, component (C) is in general added at 0.001 to 5 weight parts per 100 weight parts component (A).

The platinum-group metal catalyst comprising component (D) of the present invention is a catalyst for crosslinking and curing of components (A) and (B). This component is exemplified by chloroplatinic acid, alcohol-modified chloroplatinic acid, chloroplatinic acid/olefin complexes, chloroplatinic acid/vinylsiloxane complexes, microparticulate platinum adsorbed on a particulate carbon carrier, platinum black, palladium catalysts, and rhodium catalysts. This component should be used in a catalytic quantity, that is, a quantity sufficient to effect the cure of the composition of the present invention. In order to effect curing of the composition of the present invention by brief treatment at temperatures not exceeding 100°C, this component is generally used within the range of 1 to 1,000 ppm as platinum metal per 100 weight parts component (A), and more preferably within the range of 10 to 300 ppm as platinum metal per 100 weight parts component (A).

The nonreactive organopolysiloxane comprising the optional component (E) of the present invention is a component to bring about further improvements in the release performance. After the composition of the present invention has been cured, component (E) is present in a free state in the cured product. This organopolysiloxane must not contain silicon-bonded alkyl groups nor silicon-bonded hydrogen atoms. It is maybe either a liquid or gum at room temperature. Component (E) is exemplified by trimethylsiloxy-terminated dimethylpolysiloxanes; dimethylphenylsiloxy-terminated dimethylpolysiloxanes; and trimethylsiloxy-terminated dimethylsiloxane-methylphenylsiloxane copolymers. Trimethylsiloxy-terminated dimethylpolysiloxanes are preferred. Component (E), when used is added at 0 to 200 weight parts per 100 weight parts component (A), and preferably at 1 to 150 weight parts per 100 weight parts component (A).

The release film-forming organopolysiloxane composition of the present invention can be prepared simply by mixing the above-described components (A), (B), (C), and (D), or optionally components (A) through (E), to homogeneity. In the case of application to the surface of a sheet-form substrate such as paper, synthetic film, and polyethylene-laminated kraft paper, the release film-forming organopolysiloxane composition of the present invention may be used directly, or diluted with an organic solvent. Organic solvents capable of dissolving the instant composition are exemplified by aromatic hydrocarbons such as toluene, xylene, and benzene; by hydrocarbons such as heptane and hexane; and by chlorinated hydrocarbons such as trichloroethane and perchloroethane.

The present invention is explained in greater detail below through illustrative examples. In these examples, "parts" denotes "weight parts", the viscosity is the value at 25°C, and "cs" is an abbreviation for centistokes. The curability, adherence, release resistance, and residual adhesiveness were measured by the following methods.

The organopolysiloxane release composition was coated to a thickness of approximately 1 micrometer (solids basis) on the surface of polyethylene-laminated kraft paper. The cured film was produced by heating this in a hot-air circulation drier at the specified temperature. Curability and adherence of the resulting cured film was then determined. The surface of the cured film was then forcibly rubbed with a finger 10 times (1 time = 1 back-and-forth motion).

Dulling (smearing) was determined by coating the composition in a similar manner on the surface of a substrate and then curing the composition by heating. The surface of the obtained cured coating was then rubbed with a finger. The coating was determined to be unsatisfactory when cloudiness (smear) was observed after rubbing the surface of the cured coating. Delamination (rub off) was determined by vigorously rubbing the coating with the index finger and noting that the coating could not be removed from the paper. If rub off did occur, the adherence of the coating to the substrate was determined to be unsatisfactory.

The organopolysiloxane release composition was coated to a thickness of approximately 1 micrometer (solids basis) on the surface of polyethylene-laminated kraft paper. The cured film was produced by heating this in a hot-air circulation drier at 90°C for 30 seconds. The surface of the cured film was then coated with 25 g/m² (solids basis) of a rubber-based solvent-type pressure-sensitive adhesive (Orbine BPS2411, product of Toyo Ink Seizo Kabushiki Kai-sha) followed by heating for 2 minutes at 100°C. To fabricate the measurement specimen, the treated surface was subsequently overlaid with backing paper (weight = 55 g/m²) and this assembly was aged for 10 days at 25°C under a load of 20 g/cm². This measurement specimen was then cut to a width of 5 cm to give a test specimen. Using a tensile tester, the force (g) was measured that was necessary for tensile peeling of the backing paper from the test specimen at 180° and a tensile velocity of 30 cm/minute.

A cured film of the organopolysiloxane composition was formed on the surface of polyethylene-laminated paper.
by the same method as for the release resistance test. Polyester tape (Polyester Tape 31B, brandname of Nitto Denko Kabushiki Kaisha) was then adhered on the surface of the cured film. A load of 20 g/cm² was placed on this assembly and it was heated for 20 hours at 70°C. The tape was then peeled off and re-adhered on a stainless steel plate using a 2 kg rubber roller. The adhesive force (g) was subsequently measured by peeling off the tape using a tensile tester. Residual adhesiveness was measured using the following formula:

\[
\text{residual adhesiveness (\%)} = \left(\frac{\text{residual adhesive force}}{\text{initial adhesive force}}\right) \times 100
\]

**EXAMPLE I**

The following were placed in a condenser-equipped 1,000 mL flask: 63 g (grams) trimethylsiloxy-terminated methylhydrogenpolysiloxane with viscosity = 40 mm²/s (cs), 4 g trimethylsiloxy-terminated methylolpolysiloxane with viscosity = 120 mm²/s (cs), 33 g octamethylcyclotetrasiloxane, and 3 g activated clay. An equilibration reaction was then run by heating for 5 hours at 80°C while stirring under a nitrogen current. Filtration of the reaction product yielded 75 g trimethylsiloxy-terminated dimethylsiloxane-methylolpolysiloxane-methylhydridesiloxane copolymer with viscosity = 100 mm²/s (cs). The following were then dissolved in 700 weight parts toluene: 100 weight parts silanol-terminated dimethylsiloxane-hexylmethylsiloxane copolymer gum (hexylmethylsiloxane unit content = 3 mol%), 20 weight parts of the trimethylsiloxy-terminated dimethylsiloxane-methylolpolysiloxane-methylhydridesiloxane copolymer prepared as described above, 0.3 weight parts 3,5-dimethyl-1-hexyn-3-ol, and 100 weight parts silanol-terminated dimethylpolysiloxane gum. The release-film forming organopolysiloxane composition was finally prepared by dissolving sufficient chloroplatinic acid/divinyltetramethyldisiloxane complex into the preceding solution to give 120 ppm as platinum metal based on the total organopolysiloxane weight. The curability, adherence, release resistance, and residual adhesiveness were measured on this composition, and the results are reported in Table I.

**EXAMPLE II**

The following were placed in a condenser-equipped 1,000 mL flask: 63 g trimethylsiloxy-terminated methylhydrogenpolysiloxane with viscosity = 40 mm²/s (cs), 4 g trimethylsiloxy-terminated methylolpolysiloxane with viscosity = 120 mm²/s (cs), 33 g octamethylcyclotetrasiloxane, and 3 g activated clay. An equilibration reaction was then run by heating for 5 hours at 80°C while stirring under a nitrogen current. Filtration of the reaction product yielded 75 g trimethylsiloxy-terminated dimethylsiloxane-methylolpolysiloxane-methylhydridesiloxane copolymer with viscosity = 100 mm²/s (cs). The following were then dissolved in 700 weight parts toluene: 100 weight parts silanol-terminated dimethylsiloxane-hexylmethylsiloxane copolymer gum (hexylmethylsiloxane unit content = 3 mol%), 20 weight parts of the trimethylsiloxy-terminated dimethylsiloxane-methylolpolysiloxane-methylhydridesiloxane copolymer prepared as described above, 0.3 weight parts 3,5-dimethyl-1-hexyn-3-ol, 100 weight parts silanol-terminated dimethylpolysiloxane gum, and 10 parts trimethylsiloxy-terminated dimethylpolysiloxane. The release-film forming organopolysiloxane composition was finally prepared by dissolving sufficient chloroplatinic acid/divinyltetramethyldisiloxane complex into the preceding solution to give 120 ppm as platinum metal based on the total organopolysiloxane weight. The curability, adherence, release resistance, and residual adhesiveness were measured on this composition, and the results are also reported in Table I.

**COMPARISON EXAMPLE I**

A release-film forming organopolysiloxane composition was prepared as in Example I, but in this case using a trimethylsiloxy-terminated dimethylsiloxane-methylhydridesiloxane copolymer with viscosity = 40 (mm²/s (cs)) in place of the trimethylsiloxy-terminated dimethylsiloxane-methylolpolysiloxane-methylhydridesiloxane copolymer used in Example I. The properties of this composition were measured as in Example I, and the results are reported in Table I.

| TABLE I |
|-----------------|-----------------|-----------------|-----------------|
|                | Example I       | Example II      | Comparison Example I |
| curing conditions | 90°C 30 sec | 100°C 20 sec | 90°C 30 sec | 100°C 20 sec |
| dulling         | no             | no             | no             | no             |
| delamination    | no             | no             | no             | yes             |
|                  |                 |                 |                 | yes             |
TABLE I (continued)

<table>
<thead>
<tr>
<th></th>
<th>Example I</th>
<th>Example II</th>
<th>Comparison Example I</th>
</tr>
</thead>
<tbody>
<tr>
<td>release resistance (g/5cm)</td>
<td>9.5</td>
<td>9.2</td>
<td>9.7</td>
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<tr>
<td>residual adhesive force (%)</td>
<td>90</td>
<td>89</td>
<td>90</td>
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Claims

1. A release film-forming organopolysiloxane composition comprising:
   (A) 100 weight parts of an organopolysiloxane having at least 2 alkenyl groups of general formula \( \text{H}_2\text{C}=:\text{C}(\text{CH}_2)_n= \) in each molecule, wherein \( n \) has a value of from 2 to 8;
   (B) 1 to 200 weight parts of an octyl-containing organohydrogensiloxane having at least two silicon-bonded hydrogen atoms;
   (C) an addition-reaction inhibitor, and
   (D) a catalytic quantity of a platinum group metal catalyst.

2. A composition according to Claim 1, wherein the composition further comprises (E) from 1 to 200 weight parts of a nonreactive organopolysiloxane.

3. A method of making a cured release coating, the method comprising:
   (I) mixing;
   (A) 100 weight parts of an organopolysiloxane having at least 2 alkenyl groups of general formula \( \text{H}_2\text{C}=:\text{C}(\text{CH}_2)_n= \) in each molecule, wherein \( n \) has a value of from 2 to 8;
   (B) 1 to 200 weight parts organohydrogenpolysiloxane having at least 2 silicon-bonded hydrogen atoms and at least 1 octyl group;
   (C) an addition-reaction inhibitor;
   (D) a catalytic quantity of a platinum-group metal catalyst;
   (II) applying the mixture of Step (I) to a solid substrate to form a coating; and
   (III) exposing the coating to heat in an amount sufficient to cure the coating.

4. A method according to Claim 3 wherein the method further comprises adding from 1 to 200 weight parts of a nonreactive organopolysiloxane prior to step (II).

5. A method according to Claim 3, wherein the method further comprises dissolving the mixture from step (I) in an organic solvent prior to step (II).

6. A method according to Claim 3, wherein the substrate is selected from the group consisting of paper, synthetic film, and polyethylene-laminated Kraft paper.

Patentansprüche

1. Trennflümbildende Organopolysiloxanzusammensetzung umfassend
   (A) 100 Gewichtsteile eines Organopolysiloxans, mit mindestens 2 Alkenylgruppen der allgemeinen Formel \( \text{H}_2\text{C}=:\text{C}(\text{CH}_2)_n= \) in jedes Molekül, worin \( n \) einen Wert von 2 bis 8 hat;
   (B) 1 bis 200 Gewichtsteile eines octylgruppenhaltigen Organohydrogensiloxans mit mindestens 2 silicium-
   gebundenen Wasserstoffatomen;
   (C) einen Inhibitor der Additionsreaktion und
   (D) eine katalytische Menge eines Metalls der Platingruppe als Katalysator.
2. Zusammensetzung nach Anspruch 1, worin die Zusammensetzung weiterhin (E) 1 bis 200 Gewichtsteile eines nicht reaktiven Organopolysiloxans enthält.

3. Verfahren zur Herstellung einer gehärteten Trennbeschichtung, wobei das Verfahren umfaßt, daß man

(I) die Mischung von Stufe (I) auf ein festes Substrat aufträgt unter Bildung einer Beschichtung und (II) die Beschichtung erwärmt in einem Ausmaß, das ausreicht, um die Beschichtung zu härten.

4. Verfahren nach Anspruch 3, worin das Verfahren weiterhin umfaßt, daß man 1 bis 200 Gewichtsteile eines nicht reaktiven Organopolysiloxans vor Stufe (II) zugibt.

5. Verfahren nach Anspruch 3, worin das Verfahren weiterhin umfaßt, daß man die Mischung von Stufe (I) in einem organischen Lösungsmittel löst vor der Stufe (II).


Revendications

1. Une composition à base d'organopolysiloxane pour la formation de films antiadhésifs, comprenant :

(A) 100 parties en poids d'un organopolysiloxane dont chaque molécule compte au moins 2 groupes alcényles de formule générale H₂C=CH-(CH₂)ₙ, où n a une valeur de 2 à 8 ;
(B) 1 à 200 parties en poids d'un organohydrogénosiloxane octylé comptant au moins deux atomes d'hydrogène liés au silicium ;
(C) un agent inhibiteur de réactions d'addition ; et
(D) une quantité catalytique d'un catalyseur à métal du groupe de platine.

2. Une composition selon la revendication 1, comprenant en outre (E) 1 à 200 parties en poids d'un organopolysiloxane non réactif.

3. Un procédé pour la production d'un revêtement antiadhésif durci, comprenant :

(I) le mélange

(A) de 100 parties en poids d'un organopolysiloxane dont chaque molécule compte au moins 2 groupes alcényles de formule générale H₂C=CH-(CH₂)ₙ, où n a une valeur de 2 à 8 ;
(B) de 1 à 200 parties en poids d'un organohydrogénopolysiloxane comptant au moins 2 atomes d'hydrogène liés au silicium et au moins 1 groupe octyle ;
(C) d'un agent inhibiteur de réactions d'addition ;
(D) d'une quantité catalytique d'un catalyseur à métal du groupe de platine ;

(II) l'application du mélange de l'opération (I) à un support solide pour former un revêtement ; et
(III) l'exposition du revêtement à de la chaleur en quantité suffisante pour durcir le revêtement.

4. Un procédé selon la revendication 3, comprenant en outre l'addition de 1 à 200 parties en poids d'un organopolysiloxane non réactif avant l'opération (I).
5. Un procédé selon la revendication 3, comprenant en outre la dissolution du mélange issu de l'opération (I) dans un solvant organique avant l'opération (II).

6. Un procédé selon la revendication 3, dans lequel le support est choisi dans le groupe formé par le papier, les films synthétiques et le papier kraft stratifié au polyéthylène.