

Description

The present invention relates to UV curable controlled release coating compositions utilizing an epoxy silicone fluid, a cationically polymerizable styrene compound, such as α -methyl styrene or a derivative thereof or a p-substituted styrene compound, and a photoactive aromatic onium salt, such as a diaryliodonium hexafluorometalloid salt.

Prior to the present invention, silicone release coatings were widely used to render various surfaces non-adherent. Non-adherent silicone treated paper is often used to support labels contacting a pressure-sensitive adhesive (PSA) prior to the use of such labels. In addition, non-adherent surfaces are often necessary in industrial packaging.

Silicones have been widely recognized for their value as release coatings particularly with respect to their use with PSAs. The release coating industry is also searching for ways to synthesize release coating compositions which can be converted to cured release coatings having a predictable variation in release characteristics when contacted with PSAs, referred to hereinafter as "controlled or differential release".

Certain coating compositions utilizing epoxy or acrylic functional groups as modifiers of the release properties of cured silicone resins are taught by U.S. Patent 4,576,999. UV cured epoxysilicone polymers having controlled release also are discussed in the EP-A 0 334 056 utilizing condensed organosiloxy units substituted with esterified benzoyl groups. Another method for modifying release characteristics of UV curable epoxy functional silicones is taught in U.S. Patent 4,547,431, resulting from the addition of epoxy monomers.

Controlled or differential release of organopolysiloxane resins is also discussed in the EP-A-0 355 381. Organopolysiloxanes are modified with monovalent phenolic radicals having from 6 to 26 carbon atoms, monovalent acrylic organic radicals, or monovalent epoxy functional organic radicals. These modified silicones have been found to have controlled release. The incorporation of the phenolic groups onto the organopolysiloxane backbone is achieved by an SiH to vinyl addition reaction catalyzed by a platinum catalyst. Although effective controlled release results are achieved, it has been found that residual amounts of unreacted allylphenol used to incorporate phenolic groups into the resin, often impart an undesirable phenolic odor to the silicone release resin.

Improved substantially odor free UV curable compositions are shown in the EP-A 0 404 029. The EP-A 0 404 030 discloses a method for coating substrates with UV-curable epoxy silicone compositions.

Although various UV curable epoxy silicone compositions have been provided, significant effort is being expended by the silicone industry to find additional silicone release coating compositions capable of providing silicone coatings with controlled release characteristics.

The present invention is based on the discovery that certain cationically polymerizable aromatic compounds such as, α -methylstyrenes, or a p-substituted styrene compound, for example, p-vinyl anisole, can provide effective controlled release characteristics to epoxy silicones when blended with such materials along with an effective amount of an aromatic onium salt, such as a diaryliodoniumhexafluoroantimonate salt. A substantially uniform solventless blend can be provided. Simultaneous cationic polymerization of both the epoxy silicone fluid and the cationically polymerizable alkenyl substituted aromatic compound can be achieved when the resulting blend is exposed to ultraviolet light. Unlike epoxy monomers, which can require levels of 30% by weight or greater of the release coating composition, to achieve a satisfactory controlled release effect with the epoxy silicone fluid, the cationically polymerizable styrene of the present invention can be used at 1% to 26% by weight levels of the release coating composition.

There is provided by the present invention, a UV curable controlled release composition comprising by weight,

(A) 100 parts of an epoxy silicone fluid consisting essentially of 20 to 100 condensed siloxy units which constitute 84 to 94 mole percent of diorganosiloxy units of the formula,



and 6 to 16 mole percent of epoxy organosiloxy units of the formula,



(B) from 1 to 35 parts of a cationically polymerizable styrene compound selected from α -methylstyrene compounds, p-substituted styrene compounds and mixtures thereof, and

(C) an effective amount of a photoactive aromatic onium salt,

where R is selected from the same or different $C_{(1-13)}$ monovalent organic radicals and R^1 is a

monovalent epoxy functional organic radical.

Radicals included within R are, for example, C₍₁₋₈₎alkyl radicals, such as methyl, ethyl, propyl, butyl, pentyl, alkenyl radicals such as vinyl, alkyl, cycloaliphatic radicals, for example trifluoropropyl, cyanoethyl; aryl radicals, such as phenyl, tolyl, xylyl, haloaryl, for example, chlorophenyl. Radicals included within R¹ are, for example, ethylepoxycyclohexyl, propylglycidyl ether, and 1-methyl-4-isopropyl epoxycyclohexyl.

The polyarylonium hexafluorometalloid salts which can be used in the practice of the present invention include group VIa aromatic sulfonium salts as shown by U.S. Patent 4,058,401 and U.S. Patent 4,161,478, and diaryliodonium hexafluorometalloid salts shown by U.S. Patent 4,173,551.

Some of the triarylsulfonium salts are, for example, triphenylsulfonium hexafluoroarsenate, triphenylsulfonium hexafluoroantimonate and triarylsulfonium hexafluorophosphate. Among the diaryliodonium salts which can be used are, for example, diphenyliodonium hexafluoroarsenate, and diphenyliodonium hexafluorophosphate. In addition to the aforementioned arylonium salts, there also can be used arylonium salts selected from the class consisting of hexafluorophosphates, hexafluoroarsenates and hexafluoroantimonates having at least one aryl radical substituted with a nuclear bound-OR² group, where R² is a C₍₈₋₂₀₎ alkyl radical. Reference is made to EP-A-0334 056 for Non-Toxic Aryl Onium Salts, UV Curable Coating Compositions and Packaging Use, which shows additional polyarylonium hexafluorometalloid salts which can be employed in the practice of the present invention. An effective amount of the aryl onium salts which can be used, is for example, from .1% to 2% by weight and preferably .25% to 1% by weight based on the weight of release coating composition.

Epoxy silicones used in the practice of the present invention can be made by effecting reaction between epoxide monomers having ethylenic unsaturation and an organohydrogen polysiloxane in the presence of a catalytic amount of a precious metal such as a platinum catalyst. Included within the ethylenically unsaturated epoxy monomers which can be employed to make the epoxysilicones used in the practice of the present invention are commercially available materials such as 1-methyl-4-isopropenylcyclohexene oxide, 2,6-dimethyl-2,3-epoxy-7-octene, 1,4-dimethyl-4-vinylcyclohexene oxide and vinylcyclohexene monoxide. Vinylcyclohexene oxide is the preferred ethylenically unsaturated epoxide which can be used.

Addition between the ethylenically unsaturated epoxide and the SiH functional groups of the organohydrogenpolysiloxane can be effected in accordance with the procedure shown by Eckberg U.S. Patent 4,279,717, employing an effective amount of a platinum metal catalyst. In order to maintain the desired mole percent range of epoxy functionality in the epoxy-silicone, as set forth in the Statement of the Invention, there can be used various organohydrogenpolysiloxanes which preferably are methylhydrogenpolysiloxane fluids. For example, in instances where the 10 mole percent of epoxy functionality is required, a methylhydrogenpolysiloxane having a chain length of about 100 chemically combined siloxy units consisting essentially of about 90 mole percent of dimethylsiloxy units, 8 mole percent of methylhydrogen-siloxy units chain-stopped with dimethylhydrogensiloxy units can be used. In instances where higher mole percents of epoxy functionality are desired, methylhydrogen polysiloxane having a shorter chain length of methylhydrogen siloxy units and dimethylsiloxy units and optionally having dimethylhydrogensiloxy chain-stopping units can be used. In instances where lower mole percents of epoxy functionality in the epoxy silicone are desired, methylhydrogenpolysiloxanes having longer chain lengths can be employed.

α -methyl styrene compounds which can be used as controlled release additives (CRA's) are, for example, α -methyl styrene, and α -methylstyrene derivatives, such as, o, m, or p, methyl substituted α -methylstyrene; o, m, or p, phenyl substituted α -methyl styrene; o, m, or p methoxy substituted α -methylstyrene; o, m or p, phenoxy substituted α -methylstyrene.

Among the p-substituted styrene compounds which can be used as CRA's are 4-methoxystyrene (vinyl anisole) and 4-ethoxy styrene; 4-C₍₁₋₈₎ alkyl styrene, such as, the corresponding 4-methyl, 4-ethyl and 4-propyl; 4-C₍₈₋₁₃₎ aryl styrene, such as the corresponding 4-phenyl styrene.

In the practice of the present invention, the UV curable coating composition can be made by blending together the epoxy silicone fluid, the cationically polymerizable organic compound or "CRA" and the aromatic onium salts. Although the order of the addition of the various ingredients is not critical, it is preferred to blend the epoxy silicone with the CRA prior to the incorporation of the aromatic onium salt.

It is also preferred to avoid the use of an organic solvent. The mixture can be stirred and coated onto the substrate with a Gravure roller which will facilitate the dispersion of the various ingredients. In particular situations however, a volatile organic solvent can be used, such as a mixture of equal parts of hexane and acetone.

Coating compositions of the present invention can be applied to various substrates by conventional means such as by roller coating, spraying and dip coating. The silicone release compositions can be applied, for example, on paper, metals, foils, glass, as well as polymer coated papers such as polyolefin

coated kraft paper, polyolefin films, such as polyethylene and polypropylene films and polyester films.

Cure of the applied coatings can be effected by photopolymerization of the UV curable epoxysilicone compositions upon exposure to a radiation source within the ultraviolet and visible regions. Some of the radiation sources are, for example, mercury, xenon, carbon arc and tungsten filament lamps, sunlight, etc. Exposures can be from less than one second to 10 minutes or more depending upon the materials to be polymerized and photocatalysts employed. Electron beam irradiation also can be used.

In order that those skilled in the art will be better able to practice the present invention, the following examples are given by way of illustration and not by way of limitation. All parts are by weight unless otherwise specified.

Example 1

A series of blends were prepared of 1 part of an epoxy silicone having a viscosity of 250 centipoise (250 mPas) at 25°C and consisting essentially of condensed dimethylsiloxy units and about 16 mole percent of methyl-β-(3,4 cyclohexenyl)ethyl siloxy units with 0.1 to 0.3 part of vinyl anisole. The blends were diluted to a mixture of 20% by weight solids with a solvent blend of equal parts of hexane and acetone. There was added to the mixture, sufficient diphenyliodonium hexafluoroantimonate to produce photo curable release composition having 3% by weight of the onium salt.

Coatings were applied to polyethylene kraft using a coating rod and allowed to dry. The treated paper was cured by exposure to a mercury vapor lamp at 200-300 watts/inch (7.87-11.81 W/mm) at 50 feet (15.24 m) per minute. Release numbers were obtained against an aggressive solvent cast SBR (styrene-butadiene-rubber) pressure sensitive adhesive at a pull of 300 inch/minute (7.62 m/min) at 180° angle. Release was measured in units of grams/2 in (g/50.8 mm). The following results were obtained after a shelf period of 4 weeks.

Parts of Anisole

Release (4 wks)

-	35-45
.1	55-70
.2	145-175
.3	185-225

The above results show that a variation in the weight level of vinyl anisole in the epoxy silicone composition can significantly influence the release characteristics of an aggressive solvent cast SBR pressure sensitive adhesive after a shelf period of 4 weeks.

The above example illustrates the invention.

Claims

1. A UV curable controlled release composition comprising by weight,
 - (A) 100 parts of an epoxy silicone fluid consisting essentially of 20 to 100 condensed siloxy units which constitute 84 to 94 mole percent of diorganosiloxy units of the formula,



and 6 to 16 mole percent of epoxy organosiloxy units of the formula,



(B) from 1 to 35 parts of a cationically polymerizable styrene compound selected from α-methylstyrene compounds, p-substituted styrene compounds and mixtures thereof, and

(C) an effective amount of a photoactive aromatic onium salt,

where R is selected from the same or different C₍₁₋₁₃₎ monovalent organic radicals and R' is a monovalent epoxy functional organic radical.

coated kraft paper, polyolefin films, such as polyethylene and polypropylene films and polyester films.

Cure of the applied coatings can be effected by photopolymerization of the UV curable epoxysilicone compositions upon exposure to a radiation source within the ultraviolet and visible regions. Some of the radiation sources are, for example, mercury, xenon, carbon arc and tungsten filament lamps, sunlight, etc. Exposures can be from less than one second to 10 minutes or more depending upon the materials to be polymerized and photocatalysts employed. Electron beam irradiation also can be used.

In order that those skilled in the art will be better able to practice the present invention, the following examples are given by way of illustration and not by way of limitation. All parts are by weight unless otherwise specified.

Example 1

A series of blends were prepared of 1 part of an epoxy silicone having a viscosity of 250 centipoise (250 mPas) at 25°C and consisting essentially of condensed dimethylsiloxo units and about 16 mole percent of methyl- β -(3,4 cyclohexenyl)ethyl siloxy units with 0.1 to 0.3 part of vinyl anisole. The blends were diluted to a mixture of 20% by weight solids with a solvent blend of equal parts of hexane and acetone. There was added to the mixture, sufficient diphenyliodonium hexafluoroantimonate to produce photo curable release composition having 3% by weight of the onium salt.

Coatings were applied to polyethylene kraft using a coating rod and allowed to dry. The treated paper was cured by exposure to a mercury vapor lamp at 200-300 watts/inch (7.87-11.81 W/mm) at 50 feet (15.24 m) per minute. Release numbers were obtained against an aggressive solvent cast SBR (styrene-butadiene-rubber) pressure sensitive adhesive at a pull of 300 inch/minute (7.62 m/min) at 180° angle. Release was measured in units of grams/2 in (g/50.8 mm). The following results were obtained after a shelf period of 4 weeks.

<u>Parts of Anisole</u>	<u>Release (4 wks)</u>
-	35-45
.1	55-70
.2	145-175
.3	185-225

The above results show that a variation in the weight level of vinyl anisole in the epoxy silicone composition can significantly influence the release characteristics of an aggressive solvent cast SBR pressure sensitive adhesive after a shelf period of 4 weeks.

The above example illustrates the invention.

Claims

1. A UV curable controlled release composition comprising by weight,

(A) 100 parts of an epoxy silicone fluid consisting essentially of 20 to 100 condensed siloxy units which constitute 84 to 94 mole percent of diorganosiloxo units of the formula,



and 6 to 16 mole percent of epoxy organosiloxo units of the formula,



(B) from 1 to 35 parts of a cationically polymerizable styrene compound selected from α -methylstyrene compounds, p-substituted styrene compounds and mixtures thereof, and

(C) an effective amount of a photoactive aromatic onium salt,

where R is selected from the same or different C₍₁₋₁₃₎ monovalent organic radicals and R' is a monovalent epoxy functional organic radical.



2. A UV curable controlled release composition in accordance with claim 1, where the cationically polymerizable styrene compound is vinyl anisole.
3. A UV curable controlled release composition in accordance with claim 1, where the photoactive aromatic onium salt is a diphenyliodonium hexafluoroantimonate salt.
4. A UV curable controlled release composition in accordance with claim 1, where the epoxy silicone consists essentially of condensed dimethylsiloxyl units and methyl- β -(3,4 cyclohexenylepoxy)ethylsiloxyl units.

Patentansprüche

1. UV-härtbare Zusammensetzung mit kontrollierter Freigabe, umfassend, bezogen auf das Gewicht,
 - (A) 100 Teile einer Epoxysilicon-Flüssigkeit, bestehend im wesentlichen aus 20 bis 100 kondensierten Siloxyeinheiten, die 84 bis 94 Mol-% von Diorganosiloxyl-Einheiten der Formel



und 6 bis 16 Mol-% von Epoxyorganosiloxyl-Einheiten der Formel



bilden,

(B) von 1 bis 35 Teile einer kationisch polymerisierbaren Styrol-Verbindung, ausgewählt aus α -Methylstyrol-Verbindungen, p-substituierten Styrolverbindungen und deren Mischungen und

(C) eine wirksame Menge eines photoaktiven aromatischen Oniumsalzes, worin R ausgewählt ist aus gleichen oder verschiedenen einwertigen organischen $C_{(1-13)}$ -Resten und R' ein einwertiger epoxyfunktioneller organischer Rest ist.

2. UV-härtbare Zusammensetzung mit kontrollierter Freigabe gemäß Anspruch 1, worin die kationisch polymerisierbare Styrol-Verbindung Vinylanisol ist.
3. UV-härtbare Zusammensetzung mit kontrollierter Freigabe gemäß Anspruch 1, worin das photoaktive aromatische Oniumsalz ein Diphenyliodoniumhexafluorantimonatsalz ist.
4. UV-härtbare Zusammensetzung mit kontrollierter Freigabe gemäß Anspruch 1, worin das Epoxysilicon im wesentlichen aus kondensierten Dimethylsiloxyl-Einheiten und Methyl- β -(3,4-cyclohexenylepoxy)-ethylsiloxyl-Einheiten besteht.

Revendications

1. Composition à anti-adhérence ajustée, qui peut durcir sous l'action d'un rayonnement ultraviolet, et qui comporte, en poids,

A) 100 parties de résine fluide époxy-silicone, essentiellement constituée de 20 à 100 motifs siloxy condensés, dont 84 à 94 % en moles sont des motifs de type diorganosiloxyl, de formule



et 6 à 16 % en moles sont des motifs de type époxy-organosiloxyl de formule



B) de 1 à 35 parties d'un composé styrénique polymérisable par voie cationique, choisi parmi les dérivés de l' α -méthylstyrène, les dérivés para-substitués du styrène et les mélanges de tels dérivés, et

C) une quantité efficace d'un sel d'onium aromatique photoactif, les symboles R représentant des groupes identiques ou différents, choisis parmi les radicaux organiques monovalents en C_{1-13} , et R' représentant un radical organique monovalent contenant un



groupe fonctionnel époxy.

2. Composition à anti-adhérence ajustée, qui peut durcir sous l'action d'un rayonnement ultraviolet, conforme à la revendication 1, dans laquelle le composé styrénique polymérisable par voie cationique est un vinyl-anisole.
3. Composition à anti-adhérence ajustée, qui peut durcir sous l'action d'un rayonnement ultraviolet, conforme à la revendication 1, dans laquelle le sel d'onium aromatique photoactif est de l'hexafluoroantimoniate de diphényl-iodonium.
4. Composition à anti-adhérence ajustée, qui peut durcir sous l'action d'un rayonnement ultraviolet, conforme à la revendication 1, dans laquelle la résine époxy-silicone est essentiellement constituée de motifs diméthylsiloxo et de motifs méthyl- β -(3,4-époxy cyclohexyl)-éthyl-siloxo, tous condensés.

