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Description

The present invention relates to novel epoxy-functional fluoroisocyanates. More particularly, the present invention relates to novel epoxy-functional fluoroisocyanates which in combination with onium salt photoinitiators will form UV-curable compositions having improved cure rate at low temperatures and improved solvent and fuel resistance.

UV radiation curable compositions containing epoxy-functional silicones and onium salt photocatalysts are known in the art. Reference is made, for example, to U.S. Patent No. 4,279,717 (Eckberg et al.); U.S. Patent No. 4,576,999 (Eckberg); and U.S. Patent No. 4,640,967 (Eckberg). The epoxy-functional silicones disclosed in these patents do not contain fluorine substituents.

Although the epoxy-functional silicones disclosed in the patents recited above form excellent UV-curable compositions, it is continually desirable to provide improved UV-curable epoxy-functional compositions.

For example, it is desirable to improve the cure efficiency of UV-curable compositions.

It is also desirable to improve the solvent and fuel resistance of UV-curable compositions.

In addition, it is desirable to provide epoxy-functional silicones which are more miscible with onium salt photoinitiators than currently used UV-curable epoxy-functional compositions.

The present invention provides UV-curable compositions having the improvements listed above.

Fluoroisocyanates are also known in the art. Reference is made, for example, to U.S. Patent Nos. 4,585,846 (Evans et al.) and 4,599,347 (Bluestein). These patents disclose solvent resistant rubber compositions containing a vinyl-terminated fluoroisocyanate copolymer gum, a platinum curing agent, and a crosslinker. The fluoroisocyanate compositions taught in the patents to Evans et al. and to Bluestein are room temperature vulcanizable compositions.

The present invention is based on the discovery that epoxy-functional fluoroisocyanates having the structural formulas described hereinafter will form UV-curable compositions having improved solvent resistance and faster cure at lower UV radiation levels than non-fluoro containing epoxy-functional silicones of the prior art.

The present invention provides epoxy-functional fluoroisocyanates selected from the group consisting of:

resinous epoxy-functional fluoroisocyanates having the general formula (III)

and

resinous epoxy-functional fluoroisocyanates having the general formula (IV)

wherein E represents an epoxy-functional organic group of from 2 to 20 carbon atoms, R represents an alkyl radical having from 1 to 10 carbon atoms, R' represents a perfluoroalkyl radical having from 1 to 8 carbon atoms, R" represents an alkyl radical having from 1 to 10 carbon atoms, "c" represents a number from 1 to 100, and "d" represents a...
number from 1 to 100.

The present invention is further directed to UV radiation-cureable compositions comprising an epoxy-functional fluorosilicone and an onium salt photocatalyst or combination of onium salt photocatalysts.

The epoxy-functional fluorosilicones described above will form UV-curable compositions having improved solvent and fuel resistance and faster cure at lower UV radiation levels. The high solvent and fuel resistance of the compositions of this invention make them highly suitable for use in electrical encapsulation or conformal coatings in under-the-hood automotive applications or other applications where fuel and solvent resistance are necessary.

The present invention is directed to novel epoxy-functional fluorosilicones and to UV-curable containing these epoxy-functional fluorosilicones and onium salt photocatalysts.

The epoxy-functional fluorosilicones of the present invention are selected from those having formulas (III) and (IV) above.

In formulas (III) and (IV), \( E \) represents an epoxy-functional organic group of from 2 to 20 carbon atoms. Preferably, \( E \) represents the radical

\[
\begin{array}{c}
\text{R}^1 \\
\text{R}^2
\end{array}
\]

wherein \( \text{R}^2 \) is an alkylene radical having from 1 to 10 carbon atoms, and most preferably an ethylene radical.

\( \text{R}^1 \) in formulas (III) and (IV) above is a perfluoroalkyl radical having from 1 to 8 carbon atoms. Preferably, \( \text{R}^1 \) represents a \( -\text{CF}_3 \) radical.

In formulas (I)-(IV), \( \text{R} \) and \( \text{R}^2 \) each represent an alkyl radical having from 1 to 10 carbon atoms, preferably methyl. The value for *a* is a number from 1 to 100, preferably from 1 to 20, and most preferably from 1 to 10, and *b* is a number from 1 to 100, preferably from 1 to 20, and most preferably from 1 to 10.

The epoxy-functional fluorosilicone resin of formula (III) can be prepared in the following manner. Methylidichlorosilane and 3,3,3-Trifluoropropylmethyldichlorosilane are dissolved in dry toluene while under a nitrogen blanket. Tetraethylorthosilicate is added with agitation to the resulting mixture. After addition of the orthosilicate, the mixture is stirred for 15 to 30 minutes and then added incrementally to distilled water. External cooling is applied to keep the temperature at about 40°C. When the reaction subsides to about 25°C, the mixture is allowed to phase separate. The organic phase is then washed with water until the pH is about 6. The material is then heated while agitating under a slight nitrogen purge to a temperature of about 115°C in order to remove solvent, water, and alcohol. The vessel temperature is then increased to about 150°C over a period of 2 to 3 hours and additional distillate recovered. The temperature of the mixture is then increased to 175 to 180°C, with recovery of additional distillate. The material can then be filtered with Celite 545 and Fuller's earth in order to reduce acidity down to about 10 ppm. The resulting hydride product was a clear fluid having a hydride content of 0.14% by weight, a viscosity of about 64 mPa-s (centipoise) at 25°C, and the following formula (VII)

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{O} \\
\text{Si}
\end{array}
\]

wherein \( \text{R}, \text{R}^1, \) and *c* are as previously defined.

The hydride-functional fluorosilicone resin of formula (VII) is mixed with a solution of VCHO and the rhodium catalyst, RhCl(Ph₃P)₂, wherein "Ph" represents phenyl. The mixture is brought to a temperature of from 90 to 120°C when sufficient VCHO is added dropwise to react with all silicon-bonded hydrogen groups (also referred to herein as "SiH") present in the resin and held there for 1 to 24 hours. A stabilizer, CH₃N(C₁₈H₃₇)₂, is optionally added as a 10% solution in organic solvent, e.g., toluene. The organic solvent and excess VCHO are removed, e.g., by distillation at a temperature of 70 to 140°C under a nitrogen stream. The resulting product had the formula
wherein E, R, R1, and "c" are as previously defined.

The epoxy-functional fluoro silicone of formula (IV) can be prepared as follows.

Methylhydrogen dichlorosilane and 3,3,3-trifluoropropylmethyl dichlorosilane are dissolved in dry toluene while under a nitrogen blanket. Trimethoxymethylsilane is added with agitation to the resulting mixture. After addition of the trimethoxymethylsilane is complete, the mixture is stirred for 20 to 30 minutes and then added to distilled water. External cooling is applied to keep the temperature at about 40°C. When the reaction subsides to about 28°C, the mixture is allowed to phase separate. The organic phase is then washed with water until the pH is about 6. The material is then heated while agitating under a slight nitrogen purge to a temperature of about 148°C in order to remove solvent, water, and alcohol. The vessel temperature is then increased to about 180°C over a period of 3 to 4 hours and additional distillate recovered. The material can then be treated with Calite 545 and Fuller's earth in order to reduce acidity down to about 10 ppm. The resulting hydride product had a hydride content of 0.36% by weight, a viscosity of about 28.8 mPa-s (centipoise) at 25°C, and the following formula (VIII)

wherein R, R1, R2 and "d" are as previously defined.

The hydride-functional fluoro silicone of formula (VIII) is mixed with an organic solvent and a solution of RhCl(Ph3P)3 in 4-vinylcyclohexene oxide. The mixture is brought to a temperature of from about 90 to about 120°C when sufficient VCHO is added dropwise to react with all SiH present in the silicone resin solution, and held there for 1 to 24 hours. A stabilizer, methylidicoamide in toluene, can be added. The stabilized reaction mixture is then stripped of solvent in vacuo at 70 to 160°C. The resulting product has the formula
wherein R, R', R", E, and "d" are as described previously herein.

The hydrosilation catalyst used in the preparation of the epoxy-functional fluorosilicones of the present invention is a catalyst which promotes the hydrosilation reaction between the VCHO and the hydride-functional fluorosilicone. Useful catalysts for facilitating the hydrosilation curing reaction include precious metal catalysts such as those which use ruthenium, rhodium, palladium, osmium, iridium, and platinum, and complexes of these metals. Examples of suitable hydrosilation catalysts are disclosed, for example, in U.S. Patent Nos. 3, 159,601 and 3, 159,662 (Ashby); 3,220,970 (Lamoreaux); 3,814,790 (Karstedt); 3,516,946 (Modic), and 4,029,629 (Jeram); all of the foregoing patents being hereby incorporated by reference herein. A preferred rhodium catalyst is Wilkinson's Catalyst which has the formula RhCl([P(Ph3)2], wherein "Ph" is phenyl.

Preferably, the hydrosilation catalyst used in the present invention is a platinum-containing catalyst. Suitable platinum-containing hydrosilation catalysts include any of the well known forms of platinum that are effective for catalyzing the reaction of silicon-bonded hydrogen atoms with silicon-bonded vinyl groups, such as finely divided metallic platinum, platinum on a finely divided carrier such as alumina, compounds of platinum such as chloroplatinic acid and complexes of platinum compounds.

Other suitable platinum-containing hydrosilation catalysts for use in the preparation of the epoxy-functional fluorosilicones of the present invention include the platinum hydrocarbon complexes described in U.S. Patent Nos. 3,159,601 and 3,159,662 to Ashby, and the platinum alcoholate catalysts described in U.S. Patent No. 3,220,970 to Lamoreaux, as well as the platinum catalysts of U.S. Patent No. 3,814,730 to Karstedt. Additionally, the platinum chloride-olefin complexes described in U.S. Patent No. 3,516,946 to Modic are also useful herein. All of the aforesaid catalysts are thermally activated. Also useful are the photoactive platinum catalysts such as those of U.S. Patent No. 4,510,094 to Drahnan. All of the U.S. Patents cited in the instant paragraph are incorporated by reference into the present disclosure.

Preferably, the platinum-containing hydrosilation catalyst is that disclosed in U.S. Patent No. 3,814,730 to Karstedt, which is hereby incorporated by reference herein. This catalyst, which is hereinafter referred to as the "Karstedt catalyst", is derived from chloroplatinic acid which has been treated with tetramethyldivinylidisiloxane.

The present invention is further directed to UV curable compositions containing any one of the epoxy-functional fluorosilicones of the present invention in combination with a catalytic amount of an onium salt photoinitiator or combination of onium salt photoinitiators.

Onium salt photoinitiators suitable for use in this invention include those having the formulae:

\[ R^3O\cdot MXn^- \]
\[ R^2S\cdot MXn^- \]
\[ R^3P\cdot MXn^- \]
\[ R^2N\cdot MXn^- \]

where radicals represented by \( R^2 \) can be the same or different organic radicals from 1 to 30 carbon atoms, including aromatic carboxyl radicals of 6 to 20 carbon atoms which can be substituted with from 1 to 4 monovalent radicals selected from C(1-18)alkoxy, C(1-8)alkyl, nitro, chloro, bromo, cyano, carboxy, mercapto, and the like, and also including aromatic heterocyclic radicals including, e.g., pyridyl, thiophenyl, pyranyl, and the like, and MXn- is a non-basic, non-nucleophilic anion, such as BF4-, PF6-, AsF6-, SbF6-, SbCl6-, HSO4-, ClO4-, and the like.

The preferred onium salts for use herein are the diaryliodonium salts. Examples of suitable diaryliodonium salts are disclosed, for example, in U.S. Patent No. 4,882,201, which is incorporated herein by reference. Specific examples of other suitable diaryl iodonium salts include 4-octyloxyphenylphenyl-iodoniumhexafluoroantimonate, bis(dodecyl
phenyliodonium hexafluoroarsenate and bis(dodecyl phenyl)iodonium hexafluoroantimonate. The most preferred of these iodonium salts is 4-octyloxyphenylphenyl-iodoniumhexafluoroantimonate.

The amount of catalyst present in the composition of this invention is not critical, so long as proper polymerization is effected. As with any catalyst, it is preferable to use the smallest effective amount possible, for the purposes herein, catalyst levels of from about 0.5%–5.0% by weight have been found suitable.

The UV-curable compositions of this invention can be prepared by combining an epoxy-functional fluorosilicone of this invention with an onium salt photoinitiator or combination of onium salt photoinitiators and exposing the mixture to an amount of ultraviolet radiation sufficient to cure the composition.

A key advantage of the UV-curable compositions of this invention is their cure efficiency. The UV-curable compositions of this invention will cure on exposure to UV radiation flux of from about 10 to about 200 millijoules/cm² for a cure time of from about 0.005 to about 0.1 seconds when two focused 118 watt/cm (300 watt/inch) medium pressure mercury vapor UV lamps are used for cure.

The present invention is further directed to articles of manufacture comprising a substrate having disposed on the surface thereof a coating containing the cured composition comprising one of the epoxy-functional fluorosilicone of the present invention and an onium salt photoinitiator or combination of onium salt photoinitiators.

The articles of the present invention are prepared by applying the curable compositions of this invention to a substrate such as a circuit board if the composition is to be used as a conformal coating, thereafter exposing the coated substrate to ultraviolet radiation sufficient to cure the composition.

In order that those skilled in the art might be better able to practice the present invention, the following examples are given by way of illustration and not by way of limitation.

Experimental

Comparison Example 1

Comparison Example 1 illustrates the preparation of a linear dimethyl-hydrogensiloxychainstopped polymethyl-3,3,3-trifluoropropyl siloxane polymer, which is useful in making the epoxyfunctional fluorosilicone.

Fluorosilicone telomeric disioxanol fluid of the formula HO[(CF₂CH₂CH₂)(CH₃)₂SiO]H (447.0 grams, 6.2 weight % OH) and reagent toluene (500.0 grams) were agitated in a flask while under a blanket of nitrogen. To this mixture were added 275 ml (88.7% reactive, 239 grams) of dimethylchlorosilane incrementally below the surface of the liquid. The reaction temperature rose from 25°C to 30°C and the mixture turned hazy with each increment of silane. The haze rapidly disappears to provide a clear solution. The addition was completed in thirty minutes and the contents of the vessel were heated to 80°C for 2 hours. Fourier Transform (i.e., computer-enhanced) infrared spectral (FTIR) of the reaction mixture displays a strong band at 2310 cm⁻¹ for SiH and no evidence of silanol at 3400 cm⁻¹. Assay of the mixture indicates HCl content of 11,520 ppm. The reaction mixture was washed seven times with equal volumes of water until free of acid. The material was then vacuum stripped on a Rofo-Vac at 50°C with water aspirator to remove the solvent and water. The resultant fluid (507.3 grams, 84% recovered yield) was found to have a hydride content of 0.15 weight %, an average degree of polymerization corresponding to about 4.3 units, a viscosity of 9 centistokes at 25°C, an N₂ of 1.3714, and a reactive hydrogen content of 0.15%. Endgroup analysis indicated the approximate molecular structure below:

(1)

To a 500 cc RB flask were added 60 grams of the fluorosilicone linear hydride of formula (1) prepared above and 60 grams of hexane. This mixture was brought to 53°C when the heating mantle was withdrawn and a solution of 11.5
grams of 4-vinylcyclohexeneoxide previously blended with sufficient amount of Karstedt's platinum catalyst to furnish 20 ppm platinum in the olefin dispersed in 20 grams of hexane were added to the hydrogen-stopped fluoroelastomer fluid over a 10 minute period. The hydroisolation reaction provided sufficient exotherm to maintain batch temperature between 53° and 56°C throughout the addition without external heating. After the complete reaction mixture was maintained at 54°C for 2 hours, FTIR examination of the reaction solution detected no SiH stretch at 2200 cm⁻¹. Hexane and unreacted VCHO were removed from the reaction product by vigorous agitation at 80°C for an hour under a strong nitrogen sweep. Sixty-six grams of a 54 centistoke viscosity fluid were ultimately isolated, having an N₂D of 1.4010. This product has the following approximate molecular structure:

![Chemical Structure](image)

100 parts of the epoxysilicone fluid of formula (2) prepared above (hereinafter referred to as “**M**D₄,RMₑ⁺”) were mixed with 1 part of a 50% solution of 4-octoxyphenylphenyl-iodoniumhexafluoroantimonate (OPPI) in 2-ethyl-1,3-hexanediol to form a clear photocurable solution. 50.8 μm (2 mil) films of this blend were found to cure to a smear-and migration-free coating with excellent adhesion to a polyethylene kraft substrate on exposure to 19 mJ/cm² focused ultraviolet light in an RPC model QC1202AN Lab UV Processor (300 watts total lamp power, 2.03 m/s (400 ft/min) conveyer speed).

**Comparison Example 2**

A linear dimethylhydrogensiloxane-chainstopped polydimethyl-3,3',3'-trifluoropropyldimethylsiloxane having a viscosity of 144 centistokes at 25°C and a hydrogen content of 0.069% was prepared according to the same procedure followed in Comparison Example 1 to prepare the fluoroelastomer linear hydride product therein. The fluoroelastomer linear hydride used in the present example is a hazy fluid with the structure below:

![Chemical Structure](image)

Sixty grams of the fluoroelastomer linear hydride of formula (4) (hereinafter referred to as “**M**H⁻R⁺(**M**⁺)”), having a hydride content of 0.041 mole hydrogen were weighed into a 500 ml flask with 0.05 grams of the Karstedt platinum catalyst plus 5.10 grams of 4-vinylcyclohexeneoxide (0.041 moles). This mixture was agitated at 80°C for 16 hours, at which time no SiH was detected via FTIR analysis. The product was devolatilized in vacuo at 120°C to afford 65 grams of a slightly hazy fluid product having a viscosity of 600 centistokes at 25°C and an N₂D of 1.3925.

Because 4-vinylcyclohexeneoxide is immiscible in the hydride-stopped fluoropolymer precursor, the improved clar-
ity of the product and the increase in fluid viscosity by 4.2 times is good evidence that the reaction product has the following structure:

100 parts of the fluoro silicone polymer of formula (5) (which is hereinafter referred to as M^{FDR} \text{H}M^F) were subsequently mixed with 1 part of a 50% solution of (4-octylphenyl)phenyl iodoniumhexafluorocantinonate (OPPI) in 2-ethyl-1,3-hexanediol, making a hazy photoreactive blend. 50.8 µm (2 mil) films of this coating mixture cured to amine- and migration-free coatings with good anchorage to polyethylene Kraft sheets upon exposure to just 19 mJ/cm² ultraviolet light flux in the RPC lab UV Processor. This result is identical to the UV flux required to cure 50.8 µm (2 mil) coatings of the epoxy-functional fluorosilicone fluid of formula (2) which is unexpected because M^{FDR} \text{H}M^F contains only one-third of the amount of reactive crosslinkable epoxy as the lower molecular weight analog contains.

The following examples illustrate that UV-curable epoxyfluorosilicone resins containing the "Q" structure are analogous to the linear epoxy-stopped fluorosilicones described previously herein in UV cure capability and in solvent resistance in the cured state despite relatively low fluorine content.

Example 1

An SiH-functional fluorosilicone resin believed to have the following structure was prepared:

The resin of the formula above is designated herein as (M^{HDR})_2QM^{H_2}. The resin contains a fluorine content of approximately 18.5% and a hydrogen content of 0.569%.

Twenty-five grams of the (M^{HDR})_2QM^{H_2} resin above (at approximately 0.115 moles of hydrogen) were weighed into a 250cc flask with 0.70 grams of a 2% solution of RhCl(Ph)_{2}P_{3} in 4-vinylcyclohexeneoxide (VCHO) catalyst solution. The mixture was brought to 105°C, when 20 grams (0.16 moles) of VCHO were added without any obvious reaction taking place. 0.2 grams of additional rhodium complex solution were added, followed by an 18 hour hold at 100°C, after which no SiH functionality was detected by FTIR analysis. 0.004 grams of (CH_{3})_{4}N(C_{18}H_{37})_{2} stabilizer were then added as a 10% solution in toluene. Toluene and excess VCHO were removed by distillation to 140°C under a nitrogen stream. 40.0 grams of product were isolated as a hazy viscous fluid, 7552 centistokes viscosity, and N_{D}^{25} of 1.4592.

The resin product was miscible with 1 weight % (4-octylxyphenyl)phenyl iodonium hexafluorocantinonate (OPPI).
50.8 μm (2 mil) coatings of photocatalyzed resin cured to smear- and migration-free glossy coatings on PEK substrate on exposure to 31 μJ/cm² UV flux. The resin is believed to have the following structure:

![Chemical Structure](image)

wherein E represents

![Chemical Structure](image)

The resin of formula (8) will hereinafter be referred to as "(MED)₂Q(MED)₂".

The solvent resistance of 127 μm (5 mil) UV-cured coatings of the epoxyfluorosilicone resin (1% OPPI) on glass was assessed as described previously herein. The one hour immersion in hexane caused only minor swelling and delamination at the bottom of the coating with no apparent effect on coating integrity at other areas directly in contact with hexane solvent.

Given the high organofunctional content and relatively low fluorine content of the epoxyfluorosilicone resin above, the observed solvent resistance is an unexpected and useful result, suggesting that these fluoroepoxysilicones are suitable for electrical encapsulation or conformal coatings where protection from solvents and fuels is required.

**Example 2**

An SiH-functional fluorosilicone resin was prepared having a hydride content of 0.35 weight % and the following formula:

![Chemical Structure](image)

The resin of the formula above is designated herein as [H(Ph₂)₂QH₂]. 28.6 grams of this SiH resin (0.1 mole H) plus 100 grams of toluene and 0.7 grams of a 0.2 weight % solution of RhCl([Ph])₂, wherein "Ph" represents phenyl, in VCHO were weighed into a 250cc flask. The solution was heated to 102°C, then agitated while 15.0 grams of VCHO (0.12 moles) were added dropwise. No evidence of exothermic reactions was observed. The complete reaction mixture was then held at 110°C for 2 hours, at which time FTIR analysis confirmed that all SiH had been reacted. Solvent and excess VCHO were removed under vacuum according 40.0 grams yield of an epoxyfluorosilicone fluid having a vis-
cosity of 242 centistokes with Nd25 of 1.4324 and the following structure

(10)

The resin of formula (10) will sometimes hereinafter be referred to as [M6(DR)2]2OME2.

The epoxysilicones fluid of formula (10) was completely miscible with 1.0 weight % of OPPi photocatalyst.

50.8 μm (2 mil) films of the catalyzed resin cured to smear- and migration- free coatings which anchored well to poly-

ethylene Kraft substrates on exposure to 16 mJ/cm² total UV fluxed generated by mercury vapor lamps in an RPC

QC1202 Lab Processor. This is an exceptionally efficient UV cure.

Examples 3 - 7

The solvent resistance of cured films of the epoxysilicones prepared in Comparative Examples 1 and 2 and in

Examples 1 and 2, respectively, and compared to a cured film of an epoxysilicone designated as M6D5E5D7OOME

having no fluorine content were studied. Each epoxysilicone was blended with 1 weight% OPPi by brief mixing at 60°C.

127 μm (5 mil) coatings of the catalyzed silicones were then manually applied to clean glass slides, then exposed to

600 mJ/cm² total UV flux in the Lab Processor unit to ensure complete cure. The coated glass slides were partially

immersed in hexane for 60 minutes, while the response of these cured coatings to this aggressive solvent was observed.

The results are shown in Table 1 below.

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Formula</th>
<th>%Fluoro</th>
<th>EEW*</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>3**</td>
<td>M6D&lt;sub&gt;4.3&lt;/sub&gt;ME</td>
<td>23.3</td>
<td>527</td>
<td>Rapid Swelling (2 min); lifts off glass (10 min). Cracking propagates to cured coating above immersion (30 min). Film completely delaminated as instact film (60 min).</td>
</tr>
<tr>
<td>4**</td>
<td>M6D&lt;sub&gt;10&lt;/sub&gt;ME</td>
<td>32.2</td>
<td>1600</td>
<td>No Deterioration (60 min.)</td>
</tr>
<tr>
<td>5</td>
<td>(M6D&lt;sub&gt;4&lt;/sub&gt;ME&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>10.6</td>
<td>276</td>
<td>No Deterioration (60 min.)</td>
</tr>
<tr>
<td>6</td>
<td>[M6D&lt;sub&gt;2&lt;/sub&gt;Q(ME)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>16.4</td>
<td>347</td>
<td>Swelling (5 min.); cracking, delaminating (10 min.); coating cracked into small pieces detached from glass up to immersion line (60 min)</td>
</tr>
<tr>
<td>7**</td>
<td>M6D&lt;sub&gt;5&lt;/sub&gt;D&lt;sub&gt;7&lt;/sub&gt;OE</td>
<td>0</td>
<td>1100</td>
<td>Complete delamination and destruction of coating (less than 1 min.)</td>
</tr>
</tbody>
</table>

* Epoxy Equivalent Weight (calculated)
** Comparative Examples

The results presented in Table 1 were surprising in that it would have been expected that the solvent resistance

of the UV-cured films would increase as a function of fluorine content.

Obviously, fluorine content alone does not dictate solvent resistance; relative *Q* content seems equally important
as the (M₄ED₃R₃)₂QMe₂ resin film proved much more resistant to attack by hexane than the (M₄ED₃R₃)₂Q(Me₆)₂ resin despite the latter having a 60% greater fluorine concentration.

Example B

28 grams of an SiH-functional fluorosilicone resin containing 0.36% reactive hydrogen, of approximate formula

(11)

(11)

(hereinafter referred to as "(M₄ED₃R₃)₂⁺") were weighed into a 250 cc flask with 100 grams of toluene and 0.2 grams of a 2 weight% solution of Wilkinson's catalyst, i.e., RhCl[(Ph)₃P]₂, in VCHO. This solution was brought to 100°C when 15 grams of VCHO were added dropwise. Following a two hour hold at 100°C, FTIR analysis detected no unreacted SiH. 0.05 grams of a 10% solution of methylidicoamine in toluene were then added, and the stabilized batch stripped of solvent and other light ends in vacuo at 160°C. The resulting clear stable product was a 95 centistoke fluid with a refractive index of 1.4262 and the formula

(12)

(12)

The resin of formula (12) will hereinafter be referred to as "(M₄ED₃R₃)₂⁺".

UV cure and solvent resistance analysis of the T-based epoxyfluorosilicone ((M₄ED₃R₃)₂⁻T resin of formula (12) was assessed as described previously herein. The extremely rapid cure response observed with other epoxyfluorosilicones was again noted here. A coating bath made up of 100/1 mix of (M₄ED₃R₃)₂⁻T/O₃P⁺ photocatalyst was a clear mixture, a 50.8 μm (2 mil) thick film of which cured to a glossy coating exhibiting no migration and excellent anchorage to polyethylene kraft substrates on exposure to 12 mJ/cm² UV flux, which is a very fast cure. 127 μm (5 mil) thick coatings of this catalyzed mixture was cured on glass slides on exposure to 600 mJ/cm² UV flux as before. This coating was partially immersed in hexane for an hour, with these observations:

1 minute: considerable swelling, no delamination

3 minute: swelling, slight delamination at bottom of coating

10 minute: same as 3 minute coating; dries out intact despite degree of swelling
30 minute: no further change

60 minute: slight delamination and cracking, but coating still intact.

The epoxyfunctional fluoro-silicone of formula (12) had an epoxy equivalent weight of 371 and a fluorine content of 15.4% by weight.

Example 9

44 grams of an SiH-functional fluoro-silicone resin containing 0.135% reactive hydrogen and having the approximate formula

\[
(13)
\]

(hereinafter referred to as \( (\text{M}^{3}\text{ED}^{12})_{2}\text{OM}^{2} \)) were weighed in a 250cc flask with 100 grams of toluene and 0.2 grams of the same VCHO solution of \( \text{RhCl} (\text{Ph}_{3} \text{P})_{3} \) as described previously. The solution was agitated at 100°C while 8 grams of VCHO were added dropwise, followed by a 2 hour hold at 105°C. Completion of this addition reaction required a second increment of rhodium catalyst solution plus an additional gram of VCHO. The reaction mixture was stabilized and devolatilized in the same fashion as \( (\text{M}^{3}\text{ED}^{12})_{2}\text{OM}^{2} \), affording 47 grams of a slightly hazy 200 centistoke viscosity fluid product having a refractive index of 1.4012 and the approximate formula

\[
(14)
\]

(hereinafter referred to as \( (\text{M}^{12}\text{ED}^{3})_{2}\text{OM}^{2} \)). Based on this formula, the product contained a fluorine content of 19.9% and had an epoxy equivalent weight of 430.

UV cure analysis was carried out on 50.8 μm (2 mil) coatings of \( (\text{M}^{3}\text{ED}^{12})_{2}\text{OM}^{2} \) and 1 weight % OPPI catalyst, which appeared to be moderately soluble in the silicone. Migration- and smear-free coatings were obtained on exposure to 14 mJ/cm² focused ultraviolet light which is a very fast rate of cure. 127 μm (5 mil) UV cured coatings of this catalyzed mixture were prepared on glass slides; immersion of the coatings in hexane resulted in no detectable degradation, swelling, nor delamination in an hour, which is equivalent solvent resistance to the highly solvent-resistant epoxyfluor-
silicone coatings described previously herein.

Claims

1. An epoxy-functional fluorosilicone selected from the group consisting of:
   resinous epoxy-functional fluorosilicones having the general formula (III)

   \[
   \begin{align*}
   \text{E} & \quad \text{Si} - \text{O} \\
   \text{Si} - \text{O} & \quad \text{Si} - \text{O} \\
   \text{R} & \quad \text{c} \\
   \text{R} & \quad \text{c} \\
   \text{R} & \quad \text{c} \\
   \end{align*}
   \]

   and

   resinous epoxy-functional fluorosilicones having the general formula (IV)

   \[
   \begin{align*}
   \text{E} & \quad \text{Si} - \text{O} \\
   \text{Si} - \text{O} & \quad \text{Si} - \text{O} \\
   \text{R} & \quad \text{d} \\
   \text{R} & \quad \text{d} \\
   \text{R} & \quad \text{d} \\
   \end{align*}
   \]

   wherein E represents an epoxy-functional organic group of from about 2 to about 20 carbon atoms, R represents an alkyl radical having from 1 to 10 carbon atoms, \( R^1 \) represents a perfluoroalkyl radical having from 1 to 6 carbon atoms, \( R^2 \) represents an alkyl radical having from 1 to 10 carbon atoms, \( c^* \) represents a number from 1 to 100, and \( d^* \) represents a number from 1 to 100.

2. An epoxy-functional fluorosilicone according to claim 1 wherein E represents the radical

   \[
   \begin{align*}
   \text{R}^3 & \quad \text{O} \\
   \text{R}^3 & \quad \text{O} \\
   \text{R}^3 & \quad \text{R}^3 \\
   \end{align*}
   \]

   wherein \( R^3 \) represents an alkylene radical having from 1 to 10 carbon atoms.

3. An epoxy-functional fluorosilicone according to claim 2 wherein \( R^3 \) represents an ethylene radical.

4. An epoxy-functional fluorosilicone according to claim 1 wherein \( R^1 \) represents the radical -CF₃.

5. An epoxy-functional fluorosilicone according to claim 1 wherein R represents a methyl radical.

6. An epoxy-functional fluorosilicone according to claim 1 wherein \( c^* \) represents a number from 1 to 20.

7. An epoxy-functional fluorosilicone according to claim 1 wherein \( d^* \) represents a number from 1 to 20.
8. An ultraviolet radiation-curable epoxy-functional fluorosilicone composition comprising:

(1) an epoxy-functional fluorosilicone selected from the group consisting of:
resinous epoxy-functional fluorosilicones having the general formula (III)

\[
\begin{align*}
\text{E} & \quad \text{O} \\
\text{Si} & \quad \text{R} \\
\text{O} & \quad \text{Si} \\
\text{R} & \quad \text{Si} \\
\text{R} & \quad \text{Si} \\
\text{E} & \quad \text{O}
\end{align*}
\]

and

resinous epoxy-functional fluorosilicones having the general formula (IV)

\[
\begin{align*}
\text{E} & \quad \text{O} \\
\text{Si} & \quad \text{R} \\
\text{O} & \quad \text{Si} \\
\text{R} & \quad \text{Si} \\
\text{R} & \quad \text{Si} \\
\text{R}^2 & \quad \text{Si}
\end{align*}
\]

wherein E represents an epoxy-functional organic group of from 2 to 20 carbon atoms, R represents an alkyl radical having from 1 to 10 carbon atoms, R¹ represents a perfluoroalkyl radical having from 1 to 8 carbon atoms, R² represents a an alkyl radical having from 1 to 10 carbon atoms, "c" represents a number from 1 to 100, and "d" represents a number from 1 to 100, and

(2) a catalytic amount of an onium salt photocatalyst or a combination of onium salt photocatalysts.

9. An epoxy-functional fluorosilicone composition according to claim 8 wherein the photocatalyst (2) is present in an amount within the range of from 0.5% to 5.0% by weight based on the weight of the epoxy-functional fluorosilicone.

10. An epoxy-functional fluorosilicone composition according to claim 8 wherein the photocatalyst (2) is a diarylido-
onium salt.

Patentansprüche

1. Epoxy-funktionelles Fluorsilicon, ausgewählt aus der Gruppe bestehend aus harzartigen, epoxy-funktionalen Flu-
orsiliconen der allgemeinen Formel (III)
und harzartigen, epoxy-funktionellen Fluorsiliconen der allgemeinen Formel (IV)

worin E eine epoxy-funktionelle, organische Gruppe mit etwa 2 bis etwa 20 Kohlenstoffatomen, R eine Alkygruppe mit 1 bis 10 Kohlenstoffatomen, R¹ einen Perfluoralkylrest mit 1 bis 8 Kohlenstoffatomen, R² einen Alkyrest mit 1 bis 10 Kohlenstoffatomen, *c* eine Zahl von 1 bis 100 und *d* eine Zahl von 1 bis 100 repräsentiert.

2. Epoxy-funktionelles Fluorsilicon nach Anspruch 1, worin E den Rest repräsentiert

worin R³ einen Alkylenrest mit 1 bis 10 Kohlenstoffatomen repräsentiert.


4. Epoxy-funktionelles Fluorsilicon nach Anspruch 1, worin R¹ den Rest -CF₃ repräsentiert.

5. Epoxy-funktionelles Fluorsilicon nach Anspruch 1, worin R einen Methylenrest repräsentiert.

6. Epoxy-funktionelles Fluorsilicon nach Anspruch 1, worin *c* eine Zahl von 1 bis 20 repräsentiert.

7. Epoxy-funktionelles Fluorsilicon nach Anspruch 1, worin *d* eine Zahl von 1 bis 20 repräsentiert.

8. Mittels UV-Strahlung härzbare, epoxy-funktionelle Fluorsilicon-Zusammensetzung, umfassend:

(1) ein epoxy-funktionelles Fluorsilicon, ausgewählt aus der Gruppe bestehend aus: harzartigen, epoxy-funktionellen Fluorsiliconen der allgemeinen Formel (III)
und harzartigen, epoxy-funktionellen Fluorsiliconen der allgemeinen Formel (IV)

worin E eine epoxy-funktionelle, organische Gruppe mit 2 bis 20 Kohlenstoffatomen, R eine Alkylgruppe mit bis 10 Kohlenstoffatomen, \( R^1 \) einen Perfluoralkylrest mit 1 bis 8 Kohlenstoffatomen, \( R^2 \) einen Alkylrest mit 1 bis 10 Kohlenstoffatomen, \( c \) eine Zahl von 1 bis 100 und \( d \) eine Zahl von 1 bis 100 repräsentiert, und (2) eine katalytische Menge eines Oniumsalz-Photo-Katalysators oder eine Kombination von Oniumsalz-Photo-Katalysatoren.

9. Epoxy-funktionelle Fluorsilicon-Zusammensetzung nach Anspruch 8, worin der photo-Katalysator (2) in einer Menge im Bereich von 0,5 bis 5,0 Gew.-%, bezogen auf das Gewicht des epoxy-funktionellen Fluorsilicons, vorhanden ist.

10. Epoxy-funktionelle Fluorsilicon-Zusammensetzung nach Anspruch 8, worin der Photo-Katalysator (2) ein Diarylodoniumsalz ist.

Reivendications

1. Fluorosilicone à groupes fonctionnels époxy, choisis dans le groupe constitué des fluorosilicones résineuses à groupes fonctionnels époxy, répondant à la formule générale:

et des fluorosilicones résineuses à groupes fonctionnels époxy, répondant à la formule générale:
formules dans lesquelles E représente un groupe organique fonctionnel époxy, ayant d'environ 2 à environ 20 atomes de carbone, R représente un groupe alkyle ayant de 1 à 10 atomes de carbone, R¹ représente un groupe perfluoroalkyle ayant de 1 à 8 atomes de carbone, R² représente un groupe alkyle ayant de 1 à 10 atomes de carbone, c représente un nombre de 1 à 100 et d représente un nombre de 1 à 100.

2. Fluorosilicone à groupes fonctionnels époxy selon la revendication 1, dans laquelle E représente le groupe de formule :

\[ \text{...} \]

dans laquelle R³ représente un groupe alkylène ayant de 1 à 10 atomes de carbone.

3. Fluorosilicone à groupes fonctionnels époxy selon la revendication 2, dans laquelle R⁰ représente un groupe éthylène.

4. Fluorosilicone à groupes fonctionnels époxy selon la revendication 1, dans laquelle R¹ représente le groupe -CF₃.

5. Fluorosilicone à groupes fonctionnels époxy selon la revendication 1, dans laquelle R représente un groupe méthyle.

6. Fluorosilicone à groupes fonctionnels époxy selon la revendication 1, dans laquelle c représente un nombre de 1 à 20.

7. Fluorosilicone à groupes fonctionnels époxy selon la revendication 1, dans laquelle d représente un nombre de 1 à 20.

8. Composition à base de fluorosilicone à groupes fonctionnels époxy, durcissable par les rayons ultraviolets, comprenant :

(1) une fluorosilicone à groupes fonctionnels époxy, choisie dans le groupe constitué des fluorosilicones résineuses à groupes fonctionnels époxy, répondant à la formule générale :
et des fluorosilicones résineuses à groupes fonctionnels époxy, répondant à la formule générale :

formules dans lesquelles E représente un groupe organique fonctionnel époxy, ayant de 2 à 20 atomes de carbone, R représente un groupe alkyle ayant de 1 à 10 atomes de carbone, R1 représente un groupe per-fluoroalkyle ayant de 1 à 8 atomes de carbone, R2 représente un groupe alkyle ayant de 1 à 10 atomes de carbone, c représente un nombre de 1 à 100 et d représente un nombre de 1 à 100, et
(2) une quantité catalytique d'un photocatalyseur qui est un sel onium, ou d'une combinaison de photocatalyseurs qui sont des sels onium.

9. Composition à base de fluorosilicone à groupes fonctionnels époxy selon la revendication 8, dans laquelle le photocatalyseur (2) est présent en une proportion comprise dans l’intervalle allant de 0,5 % à 5,0 % en poids par rapport au poids de la fluorosilicone à groupes fonctionnels époxy.

10. Composition à base de fluorosilicone à groupes fonctionnels époxy selon la revendication 8, dans laquelle le photocatalyseur (2) est un sel de diallylodonium.