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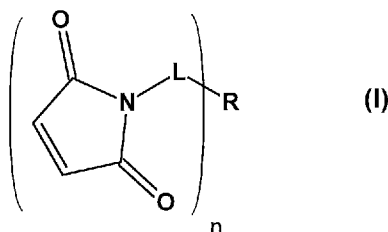
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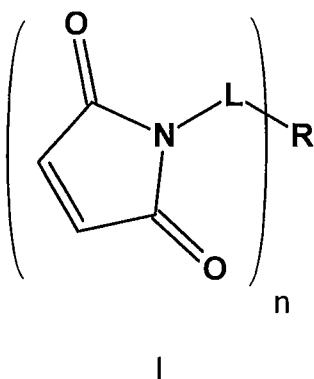
(57) Abstract: Provided herein are resins, or compounds, embraced by structure (I): where L is a covalent bond, a hydrocarbylene linker optionally having one or more hetero atoms, with or without any one or more of urethanes, ureas, amides, carbamoyls, or esters interrupting the hydrocarbylene linker; R is a backbone constructed from one or more of silicone, siloxane, urethane, ester, (meth)acrylate, amide, butadiene, hydrogenated butadiene, or olefin, which may be substituted or interrupted with ether or thioether linkages; and n is 1-10.

CURABLE COMPOSITIONS

BACKGROUND

Field

[0001] Provided herein are resins, or compounds, embraced by structure I:



where L is a covalent bond, a hydrocarbylene linker optionally having one or more hetero atoms, with or without any one or more of urethanes, ureas, amides, carbamoyls, or esters interrupting the hydrocarbylene linker;

R is a backbone constructed from one or more of silicone, siloxane, urethane, ester, (meth)acrylate, amide, butadiene, hydrogenated butadiene, or olefin, which may be substituted or interrupted with ether or thioether linkages; and

n is 1-10.

Brief Description of Related Technology

[0002] Improved surface cure (or tack-free cure) has remained a challenge to those involved in investigating UV cure chemistry, in large part because oxygen inhibits cure at the surface of a layer of an applied curable composition. Oxygen inhibition is even more pronounced in low intensity and/or longer wavelength cure processes, such as is found in UV LED or UVA cure. Use of these cure processes frequently results in tacky and uncured surfaces, even after prolonged exposure.

[0003] Several strategies have been investigated to overcome oxygen inhibition. (See e.g. Progress in Organic Coatings, 2014, 77, 1789–1798.) They include: use of chemically modified resins (see e.g. EP Patent Application Publication No. 1 698 646), additives (see e.g. US Patent Application Publication No. 2012/0083548), thiol-ene

chemistry (see e.g. US Patent No. 4,831,064), self photoinitiating resin (see e.g. EP 1 698 646), protective polymer layer (see e.g. EP Patent Application Publication No. 2 746 352), or a wax layer (see e.g. US Patent No. 9,315,695). Many of these methods suffer from disadvantages such as requiring additional processing steps, toxic additives or obnoxiously odiferous reactants.

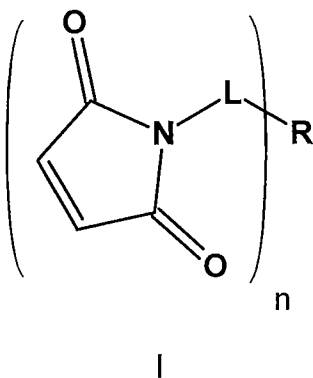
[0004] While these approaches, in principle, solve or at least minimize the problem of oxygen inhibition, they add complexity and cost to additives, process control or achieving certain technological properties of the final adhesive or coating.

[0005] Thus, it would be desirable to provide additional solutions to the problem of oxygen inhibition in UV curing adhesive or sealant systems.

SUMMARY

[0006] Such a solution is provided here in the form of a resin based approach, where resins have been designed with an architecture that mitigates oxygen inhibition during cure.

[0007] These resins, or compounds, are embraced by structure I:



where L is a covalent bond, a hydrocarbylene linker optionally having one or more hetero atoms, with or without any one or more of urethanes, ureas, amides, carbamoyls, or esters interrupting the hydrocarbylene linker;

R is a backbone constructed from one or more of silicone, siloxane, urethane, ester, (meth)acrylate, amide, butadiene, hydrogenated butadiene, or olefin, which may be substituted or interrupted with ether or thioether linkages; and

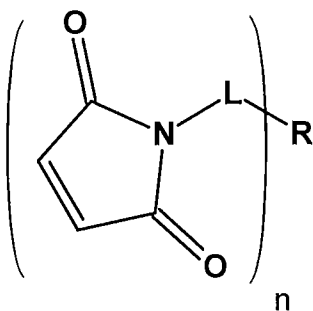
n is 1-10.

[0008] Having maleimide-containing functional groups on the backbone, such as one constructed from silicone or siloxane, leads to a resin that is radically polymerizable (aided by the presence of a curative), for instance by exposure to radiation in the electromagnetic spectrum.

[0009] Resins with a dimethylsiloxane ("DMS") backbone [such as polydimethylsiloxane ("PDMS")] may be made either by direct maleinization of amine functional silicones or by capping silane functional maleimides with α,ω -hydroxyl terminated dimethylsiloxane.

DETAILED DESCRIPTION

[0010] As noted above, the present invention provides resins, or compounds, embraced by structure I:



where L is a covalent bond or a hydrocarbylene linker optionally having one or more hetero atoms, with or without any one or more of urethanes, ureas, amides, carbamoyls, or esters interrupting the hydrocarbylene linker;

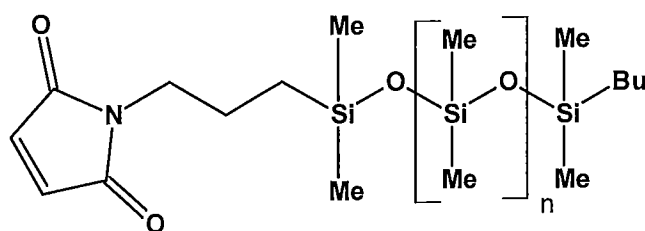
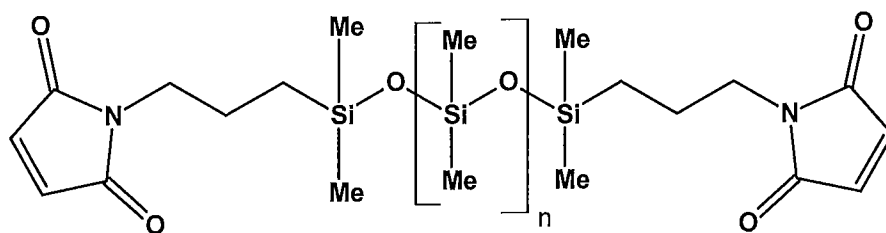
R is a backbone constructed from one or more of silicone, siloxane, urethane, ester, (meth)acrylate, amide, butadiene, hydrogenated butadiene, or olefin, which may be substituted or interrupted with ether or thioether linkages; and

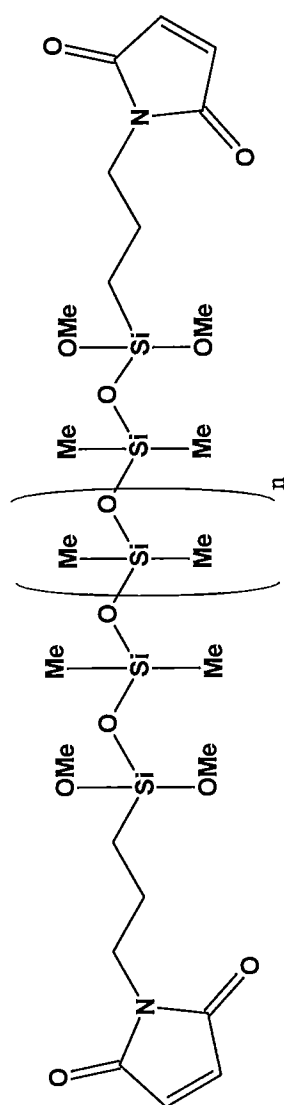
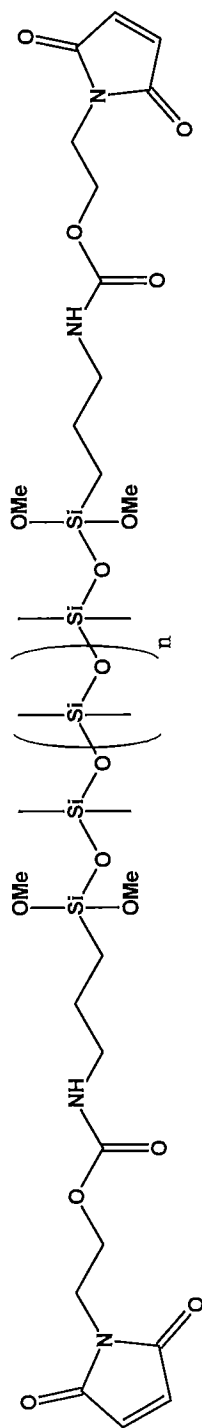
n is 1-10.

[0011] Desirably, in these compounds embraced by structure I, at least one of L or R has at least one moisture curable functional group. The moisture curable functional group may be an alkoxy silyl-containing functional group.

[0012] In addition, desirably in at least one of L or R one or more functional group(s) capable of generating radicals on exposure to radiation in the electromagnetic spectrum, such as in the visible or UV region, is(are) present.

[0013] Desirable examples of the compounds embraced by structure I include





where here n is 1-1,000.

[0014] The compounds embraced by structure I may be used to formulate a curable composition, in which case desirably a curative is also included. The curative should be at least one of a photoinitiator or a moisture cure catalyst. Ordinarily, the curative should be used in an amount of 0.01-10% by weight.

[0015] When a photoinitiator is used, it should be one that is capable of initiating cure of the composition upon exposure to radiation in the electromagnetic spectrum. Examples of appropriate photoinitiators are those that initiate cure in either or both of the ultraviolet and visible regions of the electromagnetic spectrum. For instance, UV photoinitiators, such as benzoin, benzophenone, dialkoxy-benzophenones, Michler's ketone (4,4'-bis(dimethylamino)benzophenone) and diethoxyacetophenone may be used. In addition, those UV photoinitiators available commercially under the "IRGACURE" and "DAROCUR" trade names, specifically "IRGACURE" 184 (1-hydroxycyclohexyl phenyl ketone), 907 (2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one), 369 (2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone), 500 (the combination of 1-hydroxy cyclohexyl phenyl ketone and benzophenone), 651 (2,2-dimethoxy-2-phenyl acetophenone), 1700 (the combination of bis(2,6-dimethoxybenzoyl-2,4,4-trimethyl pentyl)phosphine oxide and 2-hydroxy-2-methyl-1-phenyl-propan-1-one), and 819 [bis(2,4,6-trimethyl benzoyl)phenyl phosphine oxide] and "DAROCUR" 1173 (2-hydroxy-2-methyl-1-phenyl-1-propan-1-one) and 4265 (the combination of 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide and 2-hydroxy-2-methyl-1-phenyl-propan-1-one); and the visible light [blue] photoinitiators, di-camphorquinone and "IRGACURE" 784DC. Of course, combinations of these materials may also be employed herein.

[0016] The radiation which cures the inventive compositions may include UV and/or visible light. For visible light radiation, light-emitting diode (LED) based light generation devices may be employed. Such devices include at least one LED coupled to a power supply, which device delivers a high light output to the compositions to be cured.

[0017] Examples of light sources that can provide both UV and visible light include arc lamps. Conventional arc lamps such as mercury short arc lamps may be employed. UV curing lamp assemblies, which may include arc lamps, such as those disclosed in U.S. Pat. Nos. 6,520,663 to Holmes et al. and 6,881,964 to Holmes, the contents of which are incorporated herein by reference in their entirety, may be used.

[0018] An example of a commercially available lamp assembly useful for UV and/or visible light curing is the "ZETA 7420" (available from Henkel Corporation, Rocky Hill, CT). The

"Zeta 7420" includes a glass filter to reduce short and medium wavelength lamp emissions. The assembly can emit light in the visible blue and green region.

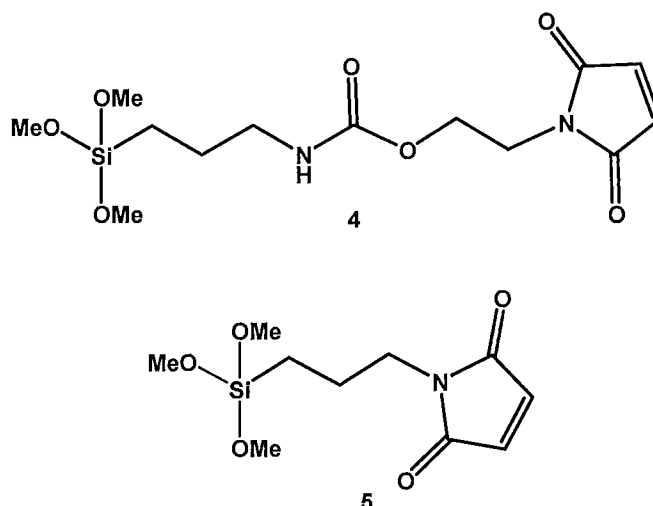
[0019] The curative may also be a moisture cure catalyst, which should be capable of initiating cure of the composition upon exposure to moisture. A common example of a moisture cure catalyst is based on the element, tin, such as dibutyltin dilaurate.

[0020] The composition after exposure to radiation in the ultraviolet region of the electromagnetic spectrum forms a tack-free surface. Such a tack-free surface may be formed in as short a period of time as about 1 second, or slightly longer. Many variables come into play when determining the time to achieve a tack-free surface. For instance, the source of the radiation, the wavelength of the radiation emitted by the source, the distance the source is to the surface receiving the radiation exposure, the time of the radiation exposure, and of course the identity and amount of the photoinitiator, and the overall constituents of the composition.

[0021] Other materials should also be used in the compositions. For instance, curable monomers may be included to modify the physical properties before, during or after cure of the composition. The monomers should be curable by free radical polymerization; chief among such monomers are (meth)acrylates. The (meth)acrylate monomers may be mono-, di- or poly-functional having one, two or many (meth)acrylate functional groups. The monomers may also be of the moisture curable variety, such as those monomers having one or more alkoxysilyl functional group(s). In such case, the compositions should also include moisture cure stabilizers to ensure an appropriate open time or good worklife.

[0022] The composition may be used as a liquid optically clear adhesive or a medical adhesive used to assembly medical devices or equipment used in support of the delivery of medical services, such as needle bonders and tube sets.

[0023] To facilitate the synthesis of bismaleimide silicones by end capping of silane functional maleimides with hydroxyl terminated PDMS, two end capping agents **4** and **5** shown below were made.



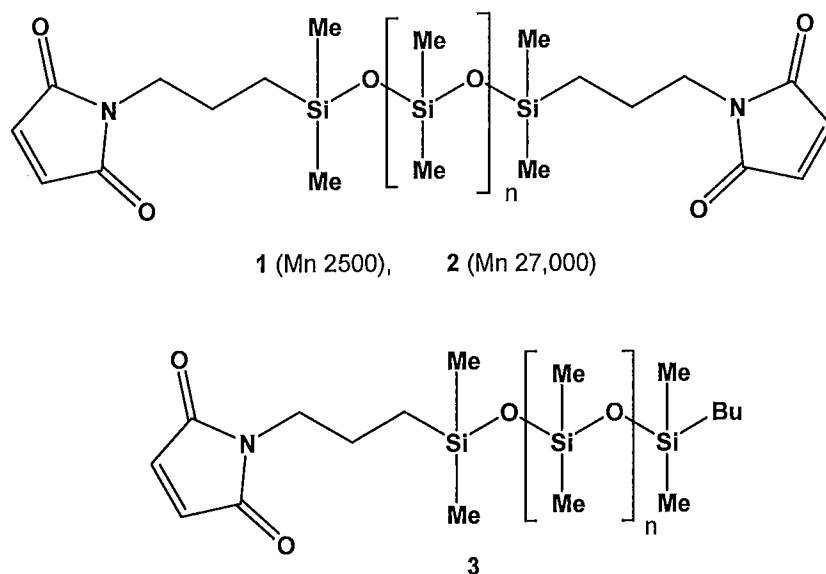
[0024] Compound **4** was made by the addition of 2-hydroxyethylmaleimide to isocyanatopropyltrimethoxy silane while compound **5** was made by maleinization of 3-aminopropyltrimethoxysilane with maleic anhydride. Two processes were developed for the synthesis of silane **5**.

[0025] The two trimethoxysilyl compounds **4** and **5** were subsequently used for capping of α,ω -hydroxyl terminated polydimethylsiloxane to obtain the corresponding maleimide functional silicone resins **6** and **7**, respectively, by an amine catalysed process.

EXAMPLES

Synthesis

[0026] Two bismaleimide silicone resins **1** and **2** of two different molecular weights and a monofunctional maleimide **3** were made by direct maleinization of corresponding aminopropyl terminated silicones with maleic anhydride in a one-pot process.



[0027] The synthesis of these resins is described in more detail below, where characterization was performed by ^1H NMR and GPC analytical techniques. The presence of maleimide end groups and complete consumption of amine functionality were established by ^1H NMR.

Synthesis of bismaleimide silicone resin 1 (Mn = 2,500)

[0028] To a 500 mL, 3 necked flask equipped with a nitrogen inlet, reflux condenser and magnetic stir bar was added maleic anhydride (4.02 g, 41 mmol) in 2-methyl THF (250 mL). A solution of aminopropyl terminated PDMS (supplied by Gelest, Mn = 2500, 50g, 20mmol) in 2-methyl THF (50mL) was added slowly dropwise over a period of 10 minutes and stirred for 2 hours at the same temperature. Zinc bromide (10.8g, 66mmol) was added under nitrogen atmosphere and the reaction was heated to 40°C. Hexamethyldisilazane ("HMDZ") (11.62g, 71mmol) in 2-methyl THF (25mL) was added slowly dropwise over a period of 45 minutes. After the addition was complete, the reaction was allowed to reflux for 2h 30 minutes and then allowed to cool to room temperature. After filtration, additional 400mL of 2-methylTHF was added, and the organic layer washed once each with water, aq. NaHCO_3 , water and dried over anhydrous Na_2SO_4 . The solution was stirred further with 10wt% silica gel for 1h, filtered and the solvent evaporated affording the maleimide terminated silicone resin **1** (32g, 63%).

Synthesis of bismaleimide silicone resin 2 ($M_n = 27,000$)

[0029] To a 500mL 3 necked flask equipped with a nitrogen inlet, reflux condenser and magnetic stir bar was added aminopropyl terminated silicone (supplied by Gelest, $M_n = 27,000$, 89.12g, 3mmol) in ethyl acetate (250mL). Maleic anhydride (0.66g, 6mmol) was added at once and stirred for 1h at the same temperature. Zinc bromide (1.81g, 8mmol) was added under nitrogen atmosphere and the reaction was heated to 40°C. HMDS (2.48mL, 11mmol) was added slowly dropwise over a period of 15 minutes. After the addition was complete, the reaction was heated at 70°C for 5h. Most of ethyl acetate was stripped off and 250mL of heptane was added followed by 10g of silica gel. The mixture was stirred for 1h and filtered off using 8 μ Whatmann filter paper. The silica was washed further with 100mL of heptane. The filtrate was passed through 0.4u filter pad and the solvent was stripped away affording silicone BMI resin 2 (72g, 81%).

Synthesis of monofunctional maleimide silicone 3 ($M_n = 1,000$)

[0030] To a 500mL 3 necked flask equipped with a nitrogen inlet, reflux condenser and magnetic stir bar was added maleic anhydride (10.26g, 104mmol) in 1-methyl THF (400mL). A solution of aminopropyl terminated PDMS ($M_n = 1000$, 99.7g, 99mmol) in 1-methyl THF (100mL) was added slowly over a period of 10 minutes and stirred for 2h at the same temperature. Zinc bromide (26.9g, 119mmol) was added under nitrogen atmosphere and the reaction was heated to 40°C. HMDZ (29g, 179 mmol) in 2-methyl THF (50mL) was added slowly dropwise over a period of 45 minutes. After the addition was complete, the reaction was stirred at 70°C for 1h and allowed to cool to room temperature. After filtration, additional methyl THF (200mL) was added and the organic layer washed with water, aq. NaHCO₃, water and dried over anhydrous Na₂SO₄. The solvent was evaporated to give monofunctional maleimide silicone 3 as an oil (80g, 80%).

Synthesis of maleimide functional silane capping agent 4

[0031] In a 250mL 3 necked flask equipped with a magnetic stir bar and nitrogen inlet was taken isocyanatopropyltrimethoxysilane (20.94g, 102mmol) in toluene (150mL). Under nitrogen atmosphere, this mixture was heated to 50°C and two drops of dibutyltin dilaurate was added. 2-hydroxyethylmaleimide (14.4g, 102mmol) was added in portions. The temperature varied in the range 50-58°C during the addition. Initially there was drop in temperature during the addition but the temperature then increased due to urethane formation. After the addition was complete, an IR was run on the sample and it showed near complete disappearance of the isocyanate band. There were peaks at 3300cm⁻¹ for the urethane NH, and two carbonyl bands around 1700cm⁻¹ for the maleimide and the urethane carbonyls. The mixture was transferred to a 500mL flask and the solvent evaporated. During evaporation, the material solidified. The solvent was stripped off for about 2h at 53°C and cooled to r.t. under nitrogen atmosphere. 100mL of heptane was added and the contents stirred and the heptane was decanted. The operation was repeated again. Last traces of heptane was stripped of in rotovap under vacuum. This gave the maleimide functional silane **4** as a white solid (28.2g, 80%).

Synthesis of silane capping agent 5**Method I for the synthesis of 3-maleimidepropyltrimethoxysilane 5**

[0032] A 2 litter, 3-neck round bottom flask equipped with mechanical stirrer, heating mantle, sparge tube and thermometer was charged with 1L of anhydrous toluene under nitrogen protection at room temperature. 44.24 grams of maleic anhydride (0.45 mol) was charged to the flask under the protection of nitrogen, the mixture was stirred at room temperature for 30 minutes. 80.88 grams of aminopropyltrimethoxysilane (0.45 mol) in 150 ml of anhydrous toluene was drop-wisely added to the flask at room temperature. The mixture was stirred for another 90 minutes. 61.5 grams of anhydrous zinc chloride (0.45 mol) was charged into the flask at room temperature under nitrogen protection, the mixture was then stirred for 30 minutes. 109.22 grams of anhydrous hexamethyldisilazane (0.68 mol) in 150 ml of anhydrous toluene was then drop-wisely added to the flask. After 3 hour reflux, the mixture was cooled to room temperature. After filtration, the clear liquid passed through a column of

silica gel, and vacuum evaporated at 90 °C for 1 hour. The collected liquid was added to heptane, the lower layer in the separation funnel was collected and then rotary evaporated. The mixture was vacuum stripped to remove the solvent affording maleimidepropyltrimethoxysilane **5**.

Method II for the synthesis of 3-Maleimidopropyltrimethoxysilane 5

[0033] A 2 liter, 3-neck round bottom flask equipped with mechanical stirrer, heating mantle, sparge tube and thermometer was charged with 1L of anhydrous toluene under nitrogen protection at room temperature. 38.44 grams of methanesulfonic acid (0.4 mol) was charged into the flask under nitrogen protection, 40.48 grams of trimethylamine (0.4 mol) in 100 ml of anhydrous toluene was then drop-wisely added into the flask after the liquid was stirred 5 minutes at 200 rpm. The mixture was then stirred at room temperature for another 15 minutes. 39.22 grams of maleic anhydride (0.4 mol) was charged to the flask under the protection of nitrogen, the mixture was stirred at room temperature for 30 minutes. 71.72 grams of aminopropyltrimethoxysilane (0.4 mol) in 150 ml of anhydrous toluene was drop-wisely added to the flask at room temperature. The mixture was stirred for another 90 minutes at room temperature. The mixture was refluxed for 16 hours and then cooled to room temperature. The top clear layer in the flask was collected and passed a thin layer of silica gel. The mixture was vacuum stripped to remove the solvent affording maleimidepropyltrimethoxysilane **5**.

Synthesis of bismaleimide silicone resin 6

[0034] To a 1 liter, 3-neck round bottom flask equipped with mechanical stirrer, heating mantle, sparge tube and thermometer was charged 285 grams of an α,ω -hydroxyl terminated polydimethylsiloxane (having a viscosity of 750 cps, commercially available from Emerald Performance Materials). The fluid was heated to a temperature of 80 °C and vacuum was applied for 60 minutes to remove any volatile component such as water and carbon dioxide. Silane capping agent **4** (18.17 g, made in the lab) and diethylhydroxyamine (0.91 g, commercially available from Sigma-Aldrich) were sequentially added to the reactor. The mixture was maintained at a temperature of 80 °C for a period of time of 8 hours. The mixture was vacuum stripped at 80°C to

remove the volatile components, and then cooled to room temperature affording the bismaleimide silicone resin **6**.

Synthesis of bismaleimide silicone resin 7

[0035] To a 1 gallon reactor equipped with mechanical stirrer, heating/cooling jacket was charged 1533 g of an α,ω -hydroxyl terminated polydimethylsiloxane (having a viscosity of 750 cps, commercially available from Emerald Performance Materials). The reactor was heated to a temperature of 80 °C and vacuum was applied for 60 minutes to remove any volatiles. Silane capping agent **5** (66.32 g) and diethylhydroxyamine (4.8 g, commercially available from Sigma-Aldrich) were sequentially added to the reactor. The mixture was maintained at a temperature of 80°C for a period of time of 8 hours. The mixture was vacuum stripped at 80°C to remove any volatiles, and then cooled to room temperature affording the bismaleimide silicone resin **7**.

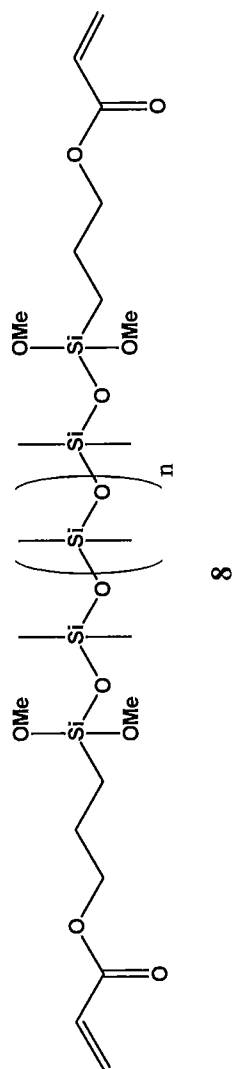
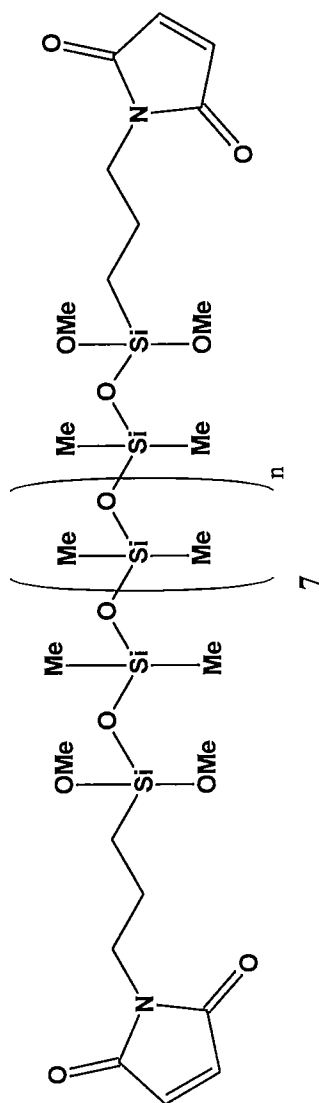
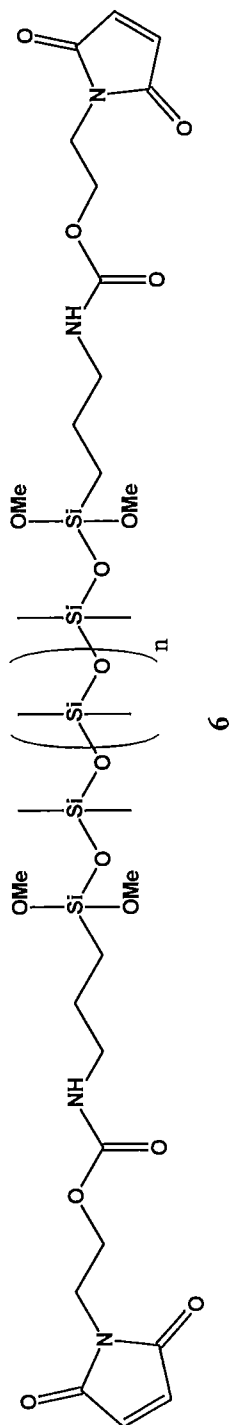
Synthesis of bismaleimide silicone resin 9

[0036] To a 100mL flask, equipped with a condenser, magnetic stirring bar, heating mantle, and thermocouple was added 1g (0.0048 mol) of N-allyl maleimide and 20mL of toluene (ACS reagent grade, >99.5%). Then 0.013g (0.01 wt%) of chloroplatinic acid hexahydrate (ACS reagent, >37.5% Pt) was added. After all catalyst was dissolved, 0.33g (0.0024 mol) of hexamethyltrisiloxane (TCI, >97%) was added dropwise, allowing for the exotherm to subside between each addition. After all of the siloxane was added, the mixture was heated at 75°C for 8 hours. The solvent was then evaporated to give the bismaleimide silicone resin **9**.

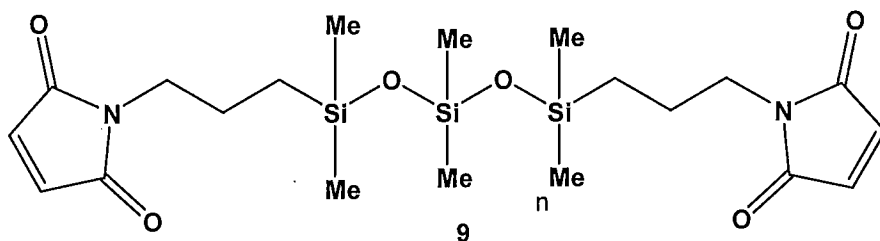
[0037] For comparative purposes to evaluate UV surface cure properties, the corresponding acrylate functional silicone resin **8** was also made by reacting acryloxypropyltrimethoxysilane with α,ω -hydroxyl terminated polydimethylsiloxane, as described below.

Synthesis of acrylate end-capped silicone resin 8

[0038] To a 1 gallon reactor equipped with mechanical stirrer, heating/cooling jacket was charged 2300 g of an α,ω -hydroxyl terminated polydimethylsiloxane (having a viscosity of 750 cps, commercially available from Emerald Performance Materials). The reactor was heated to a temperature of 60°C and vacuum was applied for 60 minutes to remove any volatiles. APTMS (109.7 g, commercially available from Gelest) and n-butyl lithium in hexane solution (1.6M; 1.85 ml, commercially available from Sigma-Aldrich) were sequentially added to the reactor. The mixture was maintained at a temperature of 60°C under vacuum for a period of time of 4 hours. Dry ice (1 g) was then added to the reaction mixture to quench the catalyst. The mixture was vacuum stripped to remove the volatile components. This gave the silicone acrylate resin **8**.



[0039] The silicone bismaleimide and monomaleimide resins can also be made by hydrosilylation reaction of N-allylmaleimide with SiH terminated silicones. To exemplify the hydrosilylation process, the hydrosilylation reaction was performed using simpler hexamethyltrisiloxane with N-allylmaleimide to give resin **9**.



Formulations

[0040] Several formulations were prepared to evaluate UV surface cure efficacy, particularly of maleimide functional silicone resins **1** and **2**. The table below summarizes the formulation components. For comparative purposes, three commercially available acrylate terminated silicone resins of different molecular weights, Silmer ACR Di10, ACR Di25 and ACR Di50, were also used.

Constituents	A	B	C	D	E	F	G	H	I	J
ACR Di10	99.88					99.86				
ACR Di25		99.89					99.85			
ACR Di50			99.88					99.86		
1				99.88	99.9				99.86	
2										99.85
IRGACURE 819	0.12	0.11	0.12	0.12	0.1	0.14	0.15	0.14	0.14	0.15

Silmer ACR Di10 Linear difunctional acrylate terminated silicone MW = 1,100, Equivalent weight = 550

Silmer ACR Di25 Linear difunctional acrylate terminated silicone MW = 1,100, Equivalent weight = 1300

Silmer ACR Di50 Linear difunctional acrylate terminated silicone MW = 4,100, Equivalent weight = 2050

UV Cure of Formulations

[0041] The formulations were exposed to radiation in the electromagnetic spectrum emitted from a Loctite-branded Zeta conveyor 7415 system (which outputs UVA 3.24, UVB 1.04, UVC 1.03, and UVV 2.34 w/cm²). Samples **A**, **B** and **C** yielded a tack-free surface when cured by exposure to UV light for up to 270 seconds. In contrast, Sample **D** -- containing the silicone bismaleimide resin **1** -- yielded a tack-free surface after being irradiated for only about 27 seconds.

[0042] The formulations were also evaluated for tack-free surface using high energy LED UV light (Phosean). After just 10 seconds of irradiation, the formulations containing silicone bismaleimide resins **1** and **2** (Samples **I** to **L** in the table below) afforded tack free surfaces while the corresponding acrylate containing formulations (Sample **F** to **H**) showed substantial transfer of resin from the surface indicating inefficient surface UV cure.

Phosean UVA 4.16 w/cm ² (High energy LED lamp)		
Resin	Sample	10 sec. irradiation
ACR Di10	F	Substantial transfer of resin from cured surface
ACR Di25	G	
ACR Di50	H	
1	I	Cured
2	J	Cured

Optical Performance of Cured Formulations after Aging Study

[0043] Adhesives and sealants destined for use in display applications should have good optical transmittance, with low visually observable color and haze. Sample **E**, containing silicone bismaleimide resin **1**, was evaluated for optical performance after aging under various elevated temperature with and without elevated moisture conditions. The results are shown in the Table below. Sample E showed good optical performance even after aging under the noted conditions for as long as 2016 hours, demonstrating suitability for use in display applications.

Sample E- 500μ Gap													
Optical test Datacolor 650	Initial	24 hours			240 hours			750 hours			2016 hours		
		85°C/ 85%	85°C	QUV	85°C/ 85%	85°C	QUV	85°C/ 85%	85°C	QUV	85°C/ 85%	85°C	QUV
		RH			RH			RH			RH		
Haze	0	1.4	0.2	0.1	5.7*	1.1	0.1	5*	1.3	0	8.6*	1.4	0
Color	0.46	1.24	1.39	1.03	1.11	1.81	1.21	1.1	1.71	0.3	1	2.3	0.12
%													
Transmittance	99.71	98.58	99.36	99.62	97.66	99.25	99.51	98.22	99.22	99.76	98.39	99.08	99.85

* Haze in center of assembly, clear surround.

UV Curing Study

[0044] Where MPMA is used as the UV light source, improved and faster tack free surface cure was achieved with silicone maleimide resins **6** and **7**, as compared to the corresponding acrylate resin **8**, none of which was formulated with a photoinitiator. Similar results were observed when a 365nm high energy LED light was used as the radiation source. The curing of formulations containing either silicone bismaleimide resins or acrylate resins was inefficient with 375nm and 405 nm low energy LED irradiation.

Photoinitiator Concentration: 0%					
Light Source*	Intensity (mW/cm ²)			Resin	Tack-Free Exposure Time (secs)
	UVA	UVB	UVV		
MPMA	128	126	74	8	75
	75	73	48	7	5
	72	72	46	6	1
365 nm LED	1890	0	0	8	> 60
				7	10
375 nm LED	62	0	19	8	> 500
				7	> 500
	98	0	36	6	> 500
405 nm LED	16	0	303	8	> 500
				7	> 500
	11	0	261	6	> 500

* MPMA light source is Loctite Zeta 7215; the LED light sources are Loctite 375 nm LED Flood System and Loctite 405 LED Flood System.

[0045] Several formulations were prepared using the silicone resins **6**, **7** and **8** by including a photoinitiator component (mixture of 70% Irgacure MBF, 20% of Irgacure 184 and 10% of Irgacure 819) and varying the photoinitiator levels.

[0046] When 0.5% by weight of photoinitiator was used, the formulations with silicone maleimide resins **6** and **7** showed tack free surfaces and curing feasibility with low energy LED irradiation (375 and 405nm). Formulations with the corresponding silicone acrylate resin **8** did not cure even after 500 seconds exposure (see table below).

Photoinitiator Concentration: 0.5%					
Light Source	Intensity (mW/cm ²)			Resin	Tack-Free Exposure Time (secs)
	UVA	UVB	UVV		
MPMA	203	189	112	8	30
	76	71	49	7	3.5
	72	72	46	6	0.5
375 nm LED	117	0	42	8	> 500
				7	240
	42	0	15	6	300
405 nm LED	13	0	278	8	> 500
				7	300
	9	0	183	6	300

[0047] When the photoinitiator level was increased to 2% by weight, the tack-free surface curing of formulations with silane functional silicone BMI resins **6** and **7** was achieved under much shorter irradiation time using low intensity UV LED light source. The corresponding acrylate resin **8** did not surface cure even after 500 seconds exposure.

Photoinitiator Concentration: 2%					
Light Source	Intensity (mW/cm ²)			Resin	Tack-Free Exposure Time (secs)
	UVA	UVB	UVV		
MPMA	75	73	47	8	25
				7	5
	72	72	46	6	0.5
375 nm LED	103	0	38	8	> 500
				7	120
	42	0	15	6	150
405 nm LED	13	0	290	8	> 500
				7	120
	5	0	114	6	75

[0048] These observations indicate the beneficial impact of the alkoxy silane and maleimide functional groups present on a silicone backbone of the resin in reducing the oxygen inhibition as compared to the corresponding acrylate **8**.

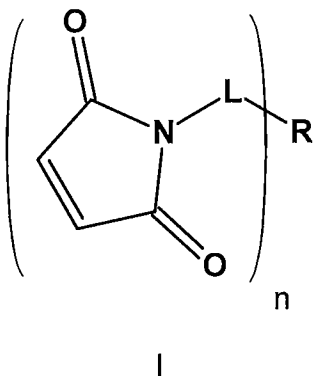
[0049] The formulations with silicone maleimide resin **6** (having a urethane linkage) appears to cure much faster than the formulations with silicone maleimide resin **7**.

[0050] The beneficial effect of alkoxy silane and maleimide groups present on the silicone backbone in reducing the oxygen inhibition in low energy UV LED cure was even more pronounced when the photoinitiator level was increased to 4% (see table below).

Photoinitiator Concentration: 4%					
Light Source	Intensity (mW/cm ²)			Resin	Tack-Free Exposure Time (secs)
	UVA	UVB	UVV		
MPMA	75	73	47	8	25
				7	10
	72	72	46	6	0.5
375 nm LED	149	0	45	8	> 500
	149	0	45	7	75
	37	0	12		300
	42	0	15	6	30
405 nm LED	16	0	309	8	> 500
	16	0	309	7	75
	15	0	262		90
	0	0	190		180
	0	0	94		300
	0	0	114	6	30

Claims:

1. A compound embraced by structure I:



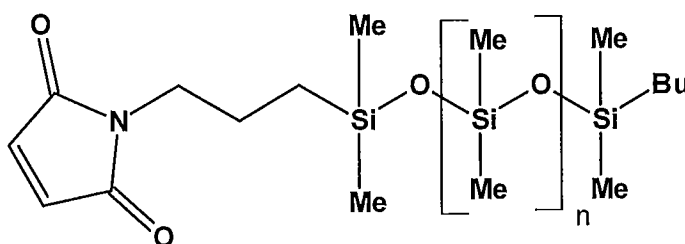
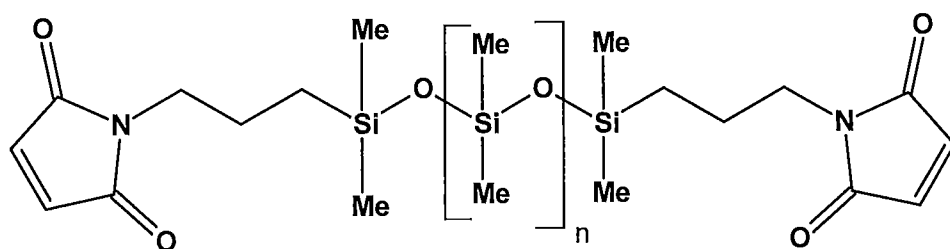
wherein L is a covalent bond, a hydrocarbylene linker optionally having one or more hetero atoms, with or without any one or more of urethanes, ureas, amides, carbamoyls, or esters interrupting the hydrocarbylene linker;

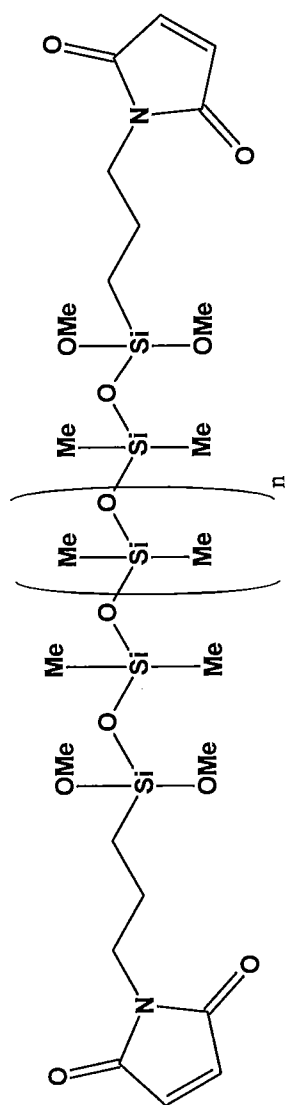
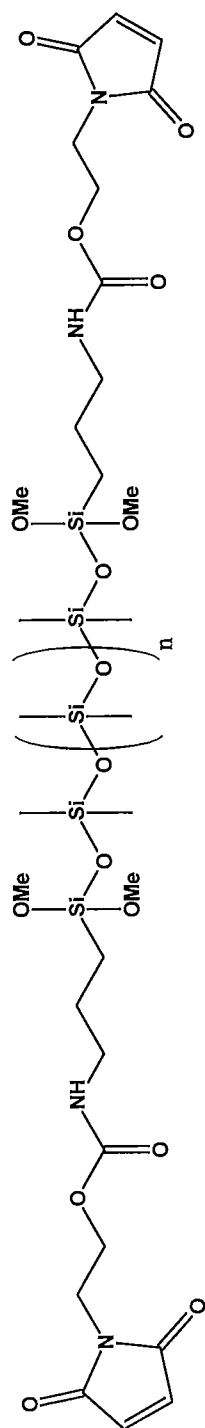
R is a backbone constructed from one or more of silicone, siloxane, urethane, ester, (meth)acrylate, amide, butadiene, hydrogenated butadiene, or olefin, which may be substituted or interrupted with ether or thioether linkages; and

n is 1-10.

2. The compound of Claim 1, wherein at least one of L or R have at least one moisture curable functional group.
3. The compound of Claim 1, wherein at least one of L or R have at least one alkoxy-silyl-containing functional group.
4. A composition comprising the compound of Claim 1 and a curative.
5. The composition of Claim 4, wherein the curative is at least one of a photoinitiator or a moisture cure catalyst.
6. The composition of Claim 5, wherein the photoinitiator is capable of initiating cure of the composition upon exposure to radiation in the electromagnetic spectrum.

7. The composition of Claim 5, wherein the photoinitiator is capable of initiating cure of the composition upon exposure to radiation in the ultraviolet region of the electromagnetic spectrum.
8. The composition of Claim 5, wherein the moisture cure catalyst is capable of initiating cure of the composition upon exposure to moisture.
9. The composition of Claim 5, wherein the moisture cure catalyst comprises tin.
10. The composition of Claim 5, wherein after exposure to radiation in the ultraviolet region of the electromagnetic spectrum a tack-free surface forms.
11. The compound of Claim 1, selected from





wherein n is 1-1,000.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2018/044767

A. CLASSIFICATION OF SUBJECT MATTER <i>C07D 207/452 (2006.01)</i> <i>C08K 5/3415 (2006.01)</i> <i>C08G 77/26 (2006.01)</i> <i>C08L 83/08 (2006.01)</i> According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C07D207/452, C08K5/3415, C08G77/26, C08L83/08 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Espacenet, DWPI, PatSearch, USPTO, RUPTO, Google, PATENTSCOPE		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 20120283378 A1 (SHOSHI M. et al.) 08.11.2012, abstract, [0016]-[0019], [0020]-[0026] [0267]-[0269], claims 1-10	1-7, 11
Y		8-10
X	JP 07032547 A (MITSUI TOATSU CHEM INC.) 03.02.1995, (abstract)	1-3
Y	CN105925037 A (CHENGDU NASHUO TECHNOLOGY CO.) 07.09.2016, (abstract)	8-10
A	EP 0586327 A2 (THREE BOND CO., LTD) 09.03.1994, (abstract, claims)	1-11
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
*	Special categories of cited documents:	“A” document defining the general state of the art which is not considered to be of particular relevance “E” earlier document but published on or after the international filing date “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) “O” document referring to an oral disclosure, use, exhibition or other means “P” document published prior to the international filing date but later than the priority date claimed “T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone “Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art “&” document member of the same patent family
Date of the actual completion of the international search		Date of mailing of the international search report
14 October 2019 (14.10.2019)		20 December 2018 (20.12.2018)
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37		Authorized officer E. Klochkova Telephone No. 8-499-240-25-91