(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 April 2019 (11.04.2019)

WIPO | PCT

(10) International Publication Number
WO 2019/070866 A1

(51) International Patent Classification:
C09J 143/04 (2006.01) *C08L 83/04* (2006.01)
C08G 77/12 (2006.01) *C08J 3/24* (2006.01)
C08G 77/14 (2006.01) *B32B 37/12* (2006.01)
C08G 77/20 (2006.01)

(21) International Application Number:
PCT/US2018/054181

(22) International Filing Date:
03 October 2018 (03.10.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/567,930 04 October 2017 (04.10.2017) US

(71) Applicants: **HENKEL IP & HOLDING GMBH** [DE/DE]; Henkelstrasse 67, 40589 Duesseldorf (DE). **HENKEL AG & CO. KGAA** [DE/DE]; Henkelstrasse 67, 40589 Duesseldorf (DE).

(72) Inventor; and
(71) Applicant *(for US only)*: **JIN, Shuhua** [US/US]; One Henkel Way, Rocky Hill, Connecticut 06067 (US).

(72) Inventors: **DECATO, Alfred A.**; 32100 Stephenson Hwy, Madison Heights, Michigan 48071 (US). **BILCAI, Eugen**; Henkelstrasse 67, 40589 Duesseldorf (DE).

(74) Agent: **PIOTROWSKI, James E.** et al.; Henkel Corporation, One Henkel Way, Rocky Hill, Connecticut 06067 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2019/070866 A1

(54) Title: DUAL CURING OPTICALLY TRANSPARENT ADHESIVE COMPOSITIONS

(57) Abstract: Two parts, dual cure, liquid optically transparent/clear adhesives having in first part A one or more vinyl-silicone-based polymer(s) and a platinum catalyst' and in a second part B optionally one or more vinyl silicone-based polymer(s); one or more (meth)acrylate end-capped silicone polymer(s); and a silicone hydride cross-linker; at least one of part A and part B includes at least one photo initiator. The mixed components, A and B, can be light cured and further cured at room temperature by platinum catalyzed addition polymerization. It is specifically useful in display panels, touch panels and optically clear adhesives.

DUAL CURING OPTICALLY TRANSPARENT ADHESIVE COMPOSITIONS

BACKGROUND

FIELD

[1] The present invention relates to liquid two part (2K)adhesive compositions which are optically transparent/clear. The adhesive compositions include one or more photocuring polymers and one or more addition curing polymers. More particularly, the present invention relates to liquid optically transparent/clear adhesives having in a first part A one or more vinyl silicone-based polymer(s) and at least one platinum catalyst; and in a second part (B) optionally one or more vinyl silicone-based polymers; one or more (meth)acrylate end-capped silicone polymer(s; and a silicone hydride cross-linker; at least one of part A and part B includes at least one photoinitiator.

[2] The present invention also relates to optical assemblies that include such optically clear adhesives. The mixed components, A and B, may be light cured and further cured at room temperature or elevated temperatures by platinum catalyzed addition polymerization (hydrosilation). It is specifically useful in display panels, touch panels and optically clear adhesives.

BRIEF DESCRIPTION OF RELATED TECHNOLOGY

[3] Liquid, optically clear or transparent adhesives ("LOCA" or "LOCAs") have been used for applications where their clarity

and transparency are needed, such as the bonding of optical lenses, display panels and touch screens to substrates. Such optical parts are commonly used on electronic devices, such as phones, computer screens and other imaging equipment. Some commercially available LOCAs, however, use a combination of photocuring and heat curing for bonding. Heat curing has disadvantages in many applications, particularly when the parts to be bonded are heat sensitive.

[4] Single component UV and moisture dual cure silicone adhesives can be cured at room temperature in the presence of moisture from air, but the curing speed is slow (more than 12 hours) and is highly dependent on the moisture availability to the material. Two-component (2K) fast addition cure materials, cured at room temperature (RTV) face the problems of short working time and gelling during dispensing. Two-component heat addition cure silicone usually requires fixture jigs to clamp the laminated parts together and then move the parts to the oven for curing. These extra steps complicate the production process, and also causes stress on the materials due to differences in temperature from heat curing, followed by cooling to room temperature.

[5] Moisture and light curable LOCAs exist; however, these LOCAs have resins based on poly (meth)acrylate backbones, which do not provide appreciable barrier properties against moisture.

[6] US Patent Application Publication No. 2015/0376476 A1 discloses an actinic radiation and moisture dual curable

composition which includes about 10 percent by weight to about 90 percent by weight of a polyolefin-based polymer, which polymer contains both moisture and photocuring functional groups, in combination with a polyolefin-based polymer which has only moisture curing functional groups.

[7] Automobile displays are particularly difficult applications not only because of their physical configurations, but also because of their environment during use; e.g. extremes of temperature. Some challenging requirements for adhesive bonding of automobile display adhesives are: 1) large shadow areas in which actinic radiation cannot penetrate, requiring an adhesive with a secondary cure mechanism, 2) small gap area making it difficult for moisture to penetrate (if the secondary cure is moisture cure), 3) good bond strength to a plastic cover lens such as PMMA, PC and PET over a broad temperature range of up to 100 C and down to -40C, 4) low haze and yellowing of the cured adhesive after exposure to high temperature, high humidity and strong UV radiation. Currently available organic (carbon hydrogen based) or silicone LOCAs do not meet all of these requirements.

[8] It would be desirable to provide a LOCA which allows for rapid primary cure, but also solves the problem of curing in shadow areas using a secondary cure mechanism, while meeting the other requirements discussed above.

SUMMARY

[9] The present disclosure provides a rapid curing

composition that can meet these challenging requirements. The disclosed composition is a liquid two-part, dual curing optically clear adhesive composition (two-part LOCA) which uses actinic radiation cure, as a primary cure mechanism, in combination with hydrosilation addition cure as a secondary cure mechanism. The term "actinic radiation" is meant to include UV light, visible light and other electromagnetic radiation capable of producing cure. The non-limiting preferred actinic radiation wavelength(nm) is form about 200 to about 500 nm. The term "addition cure" in the present invention is meant to exclude moisture cure. For clarity, the present invention is intended to overcome any reliance on moisture curing groups in favor of the actinic radiation and addition cure. In preferred embodiments, no moisture curable groups are present or alternatively if they are present, they are not relied on for curing and hence no moisture curing catalyst is present in the present inventive compositions. Thus, the present composition provides a composition which provides fast initial cure, which allows for handling and further processing, followed by a secondary cure which serves to cure any uncured composition, such as may be present in a shadow area.

[10] The two parts of the two part, dual curing adhesive composition are not storage stable once mixed and therefore must be mixed just before use, such as no more than two or three hours before use. After this time the mixed composition gels to an unusable state.

[11] Thus, in one aspect of the invention, there is provided a two part, dual curing adhesive composition which includes:

A. a first part comprising:

1) one or more vinyl silicone-based polymer(s); and

2) one or more platinum catalyst(s) for hydrosilylation cure;

B. a second part comprising:

1) optionally one or more vinyl silicone-based polymer(s)

2) one or more silicone hydride cross-linker(s); and

3) one or more (meth)acrylate end-capped silicone polymer(s);

wherein at least one of part A and part B includes at least one photoinitiator.

[12] In another aspect of the invention there is provided a process for making an optical assembly which includes the steps of:

a) providing a display panel and a top substrate comprising a cover lens or a touch panel;

b) providing the disclosed adhesive composition parts A and B and mixing these parts just before disposing the mixture between the top substrate and the display panel; and

c) initially curing the adhesive composition by exposure to radiation in the electromagnetic spectrum, and further permitting any uncured adhesive composition to cure through hydrosilylation addition-cure.

[13] In yet another aspect of the invention, there is provided an optical assembly which includes a display panel, a top substrate for the display panel and a reaction product of the disclosed adhesive composition disposed therebetween.

DETAILED DESCRIPTION

[14] This invention combines a radiation curable mechanism with an addition cure mechanism to arrive at a two-component LOCA which overcomes the problems of heat and moisture dual curing adhesive systems of the prior art. The inventive compositions contain a radiation curable silicone as a primary curing component. Advantages of radiation cure include being able to cure on command, elimination of oven curing and its attendant heat, and rapid (short) curing time (e.g., less than 60 seconds). Subsequent to radiation cure, and prior to addition cure, the laminated parts will have sufficient bonding strength to hold together, which allows the bonded parts to be handled and moved without concern that the bonded area might be negatively affected. Reaction of the mixed components provides a hydrosilylation addition cure, as a secondary cure mechanism, for any mixed composition in shadow areas that were not reachable or not exposed to actinic radiation during radiation cure.

[15] The term "liquid" as it applies to LOCAs means that the adhesive is either liquid at room temperature (25°C).

[16] The phrase "optically clear" includes low yellowness and low haze readings. For example, the colorimetry readings on a Datacolor 650 machine for the compositions of the present invention (as measured against a clear slide) would be about 0-2% for haze and desirably about 0 to less than 1% for haze; and a 0-2 value for "yellowness b", and desirably under a value of 1 for yellowness b and more desirably under a value of 0.5.

[17] LOCAs are widely used in the manufacture and assembly of touch panels and display devices to bond the cover lens, plastic or other optical materials to the main sensor unit or to each other. LOCAs tend to improve the optical characteristics of the device as well as improve other attributes such as durability. The inventive LOCAs are generally used for example to bond the touch panel to the main liquid crystal display, and also to bond any protective cover, such as the lens, to the touch panel. Commercial applications of LOCAs include the assembly and manufacture of capacitive touch panels and 3D televisions.

[18] The LOCA will be considered to be optically clear if it exhibits an optical transmission of at least about 85%. The measurement of optical transmission is known to persons skilled in the art, and may be measured on a 100 μm thick sample according to the following testing method for measuring transmission:

- placing a small drop of LOCA on a 75 mm by 50 mm plain micro slide (a glass slide from Dow Corning, Midland, MI),

that has been wiped with isopropanol and has two 100 μm thick spacer tapes attached at its two ends.

- attaching a second glass slide over the LOCA under a force.
- curing the LOCA under a UV source.
- measuring the optical transmission from wavelength 380 nm to 780 nm with a spectrometer Cary 300 from Agilent, using one blank glass slide as the background.

[19] The term "oligomer" as used herein refers to relatively low molecular weight polymeric compounds which include at least two monomer units linked to each other. Desirably the oligomer includes from 2 to 1000 monomer units linked to each other, and more desirably 2 to 300 monomer units linked to each other.

[20] The term "(meth)acryl" as used herein indicates acryl, methacryl or any combination thereof. Similarly, the term "(meth)acryloxy" indicates acryloxy, methacryloxy or any combination thereof; the term "(meth)acrylic acid" indicates acrylic acid, methacrylic acid or any combination thereof; the term "(meth)acrylate" indicates acrylate, methacrylate or any combination thereof; and the term "(meth)acrylamide" indicates acrylamide, methacrylamide or any combination thereof. The number of the (meth)acryl groups in the (meth)acrylate usable in the present invention is not particularly limited and can be one or more.

[21] The inventive adhesive compositions have a long shelf life when the components are stored separately and show good processibility, such as during lamination to form the optical

assemblies. The adhesive compositions show no yellowing after undergoing various reliability conditions. Moreover, the adhesive compositions show excellent optical performance even under harsh reliability conditions, such as extreme heat or cold.

[22] The inventive adhesive compositions are suitable for application on uneven surfaces, can be used on large and small panels, are ideal for filling in gaps, avoid condensation and fogging, provide resistance to extreme temperatures, and allow for very thin display designs.

[23] Another challenge with optical assemblies is creating an environment in which the adhesive composition may be reworked so that the LCD module or other expensive parts may be removed and reused, if a defect is discovered after the parts are assembled. For example, end-customers might return a defective display seeking a warranty repair. In such cases, the display manufacturers will want to take apart the display, remove the adhesive residue, and attempt to reuse the expensive functioning components, such as LCD modules. Therefore, one aspect of the invention is to make reworking the optical assemblies easier and more practical. The present invention also addresses this problem.

[24] The adhesive compositions of the present invention may form films which provide both the needed bonding and adhesive/sealant capabilities, as well as excellent barrier properties. In addition, the mechanical properties for the

specific intended applications are enhanced and may be tailored to take advantage of the polyolefin properties, especially the toughness and barrier properties.

[25] As recited above, Part A of the present LOCA compositions includes at least two components, namely at least one vinyl silicone and at least one platinum catalyst, but may also include other components such as photoinitiators, diluents, thickeners, stabilizers, colorants, pigments, antioxidants, plasticizers, rheology modifiers and combinations thereof, in amounts useful for their intended purpose.

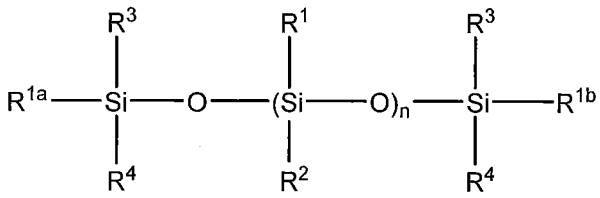
[26] Photoinitators are necessary in order for the composition to cure by actinic radiation (e.g.,photocure), such as by ultraviolet(UV) or visible light radiation. One or more photoinitiators may be present in either of (or in both) parts A and B. Photoinitiators may be present in the composition in amounts of about 0.01% to about 10.0% by weight of the part A and/or part B, desirably in amounts of about 2.0% to about 5.0% by weight of part A and/ or part B, and more desirably in amounts of about 0.2% to about 0.5% by weight of part A and/or part B. The amount of photoinitiators present by weight of the total composition (part A combined with part B) may range from about 0.01% to about 2.0%, desirably about 0.05% to about 1.0% and more desirably about 0.1% to about 0.5%.

[27] The photoinitiators useful in the present invention may be selected from any known free radical type photoinitiator effective for promoting crosslinking reactions. For example,

suitable photoinitiators include UV initiators such as benzophenone and substituted benzophenones, acetophenone and substituted acetophenones, benzoin and its alkylesters, xanthone and substituted xanthones. Desirable photoinitiators include diethoxyacetophenone (DEAP), benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, diethoxyxanthone, chloro-thioxanthone, azo-bisisobutyronitrile, N-methyl diethanolaminebenzophenone, and combinations thereof.

[28] Visible light photoinitiators include camphoquinone peroxyester initiators, non-fluorene carboxylic acid peroxyester initiators and alkyl thioxanthones, such as isopropyl thioxanthone and combinations thereof.

[29] Vinyl silicones useful in part A and include, without limitation, those conforming to structure I:



wherein where R^{1a} ,R^{1b},R1, R^2, R^3 and R^4 are each independently selected from alkyl, alkoxy, alkenyloxy, aryloxy, aryl, methacryl, methacryloxy and combinations thereof, provided that at least one of R^{1a} and R^{1b} must be a vinyl group, and desirably both R^{1a} and R^{1b} are vinyl groups. In an embodiment, three vinyl groups may be present on the structure wherein three of R^{1a}, R^{1b}, R^1, R^2, R^3 and R^4 are vinyl groups; and n is between 100 and 1,200. In one embodiment, R^1-R^4 are not moisture curing groups.

The vinyl silicone may be generally present in amounts sufficient to achieve the structural integrity required of the specific application chosen. In general, the vinyl silicone may be present in amounts of about 15% to about 90%, and desirably about 40% to about 90% by weight of part A and/or part B, and more desirably in amounts of about 60% to about 75% by weight of part A. The amount of vinyl silicone present by weight of the total composition (part A combined with part B) may range from about 10% to abou95%, desirably about 30% to about 85% and more desirably about 50% to about 70%.

[30] Useful Platinum catalyst for inclusion in part A include, without limitation, platinum or platinum-containing complexes such as the platinum hydrocarbon complexes described in U.S. Pat. Nos. 3,159,601 and 3,159,662; the platinum alcoholate catalysts described in U.S. Pat. No. 3,220,970, the platinum complexes described in U.S. Pat. No. 3,814,730 and the platinum chloride-olefin complexes described in U.S. Pat. No. 3,516,946. Each of these patents relating to platinum or platinum-containing catalysts are hereby expressly incorporated herein by reference. For example, one particularly useful platinum catalyst is Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (0.1M or 0.05M in poly(dimethylsiloxane), vinyl terminated) or Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene(Pt about 2%).

[31] The platinum catalyst may by present in sufficient amounts to provide addition cure to the dual curing composition.

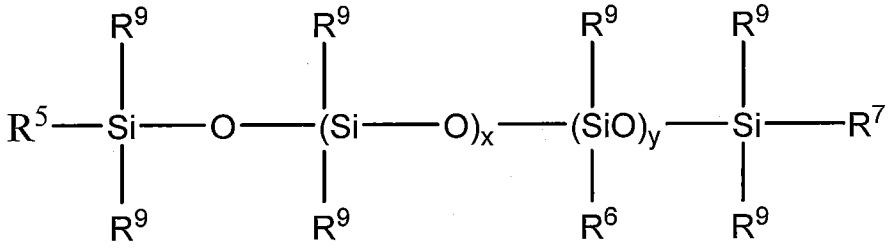
Generally, the catalyst may be present in amounts of about 0.01% to about 2.0% by weight of part A, desirably in amounts of about 0.03% to about 1.5% by weight of part A and more desirably in amounts of about 0.05% to about 1.0% by weight of part A. The amount of platinum catalyst solution present by weight of the total composition (part A combined with part B) may range from about 0.001% to about 2.0%, desirably about 0.01% to about 0.1% and more desirably about 0.05% to about 0.5%. The platinum metal wt% in the total composition is in the range of 5ppm to 500 ppm.

[32] As recited above, Part B of the present LOCA compositions includes the following components, namely: optionally at least one vinyl silicone; at least one silicone hydride crosslinker; and at least one (meth)acrylate end-capped silicone polymer, but may also optionally include one or more components selected from photoinitiators, diluents, thickeners, stabilizers, colorants, pigments, antioxidants, plasticizers, rheology modifiers and combinations thereof.

[33] Desirably, part B includes least one vinyl silicone polymer(s) which may be selected from the same group of vinyl silicone polymers as used in part A. The specific selection of silicone polymers for parts A and B may be the same or different depending upon the specific properties desired and and/or the specific end-use applications. In some aspects of the invention, the vinyl silicone polymers used in part A and/or part B may also include one or (meth)acrylate groups in addition to the vinyl group. For example, if a desired hardness is desired, the molecular weight or the degree of functionality may

be varied by selection of a particular vinyl silicone polymer. In general, the vinyl silicone may be present in each of part A and/or part B in amounts of about 15% to about 90%, and desirably about 40% to about 90% by weight in each of part A and/or part B, and more desirably in amounts of about 50% to about 70% by weight in each of part A and/or part B.

[34] Also present in part B is at least one silicone hydride crosslinker component. The crosslinker component may be present in amounts sufficient to substantially fully crosslink the vinyl silicones in part A and B which did not photocure. Silicon hydride cross-linkers useful in part B include, without limitation, those conforming to the structure II:

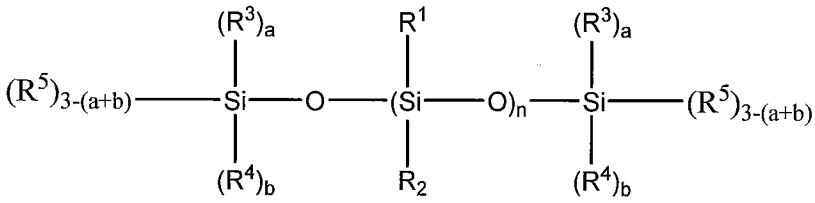


II

wherein at least two of R^5, R^6 and R^7 are H; and the other of R^5, R^6 and R^7 can be a substituted or unsubstituted hydrocarbon radical from C_{1-20} such hydrocarbon radicals including those as previously defined for formula I above; thus the SiH group may be terminal, pendent or both. R^9 can be a substituted or unsubstituted hydrocarbon radical from C_{1-20} such hydrocarbon radicals including those as previously defined for R^5, $R^6$and R^7, and desirably is an alkyl group such as methyl; x is an integer

from 10 to 1,000; and y is an integer from 1 to 20. Desirably R groups which are not H are methyl. The silicon hydride crosslinker may be present in amounts sufficient to achieve the desired amount of crosslinking and desirably in amounts of about 1 to about 10% by weight of the part B, more desirably in amounts of about 2% to about 8% and most desirably on amounts of about 3% to about 5%.

[35] Part B of the inventive compositions include a silicon polymer having at least one (meth)acrylate group and desirably with two (meth)acrylate groups. For example, the following Structure III is a non-limiting example of useful structures:

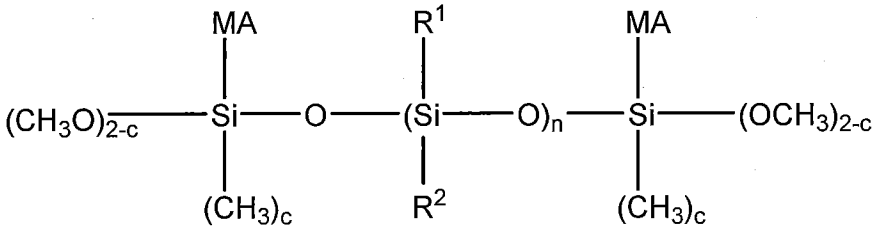


wherein R^1, R^2, R^3 and R^4 may be the same or different and are monovalent hydrocarbon radicals having up to 10 carbon atoms (C_{1-10}) or halo or cyano substituted hydrocarbon radicals; R^3 may also be a monovalent heterohydrocarbon radical having up to 10 carbon atoms (C_{1-10}) where the hereto atoms are selected from halo atoms, O, N, and S; R^5 is alkoxy (C_{1-10}), such as methyloxy, ethyloxy, isopropoxy or (meth)acryloxypropyl group; R^5may also include an ether linkage, such as $CH_2CH_2OCH_3$;however, at least one R^3 or one R^5 is a (meth)acryloxyalkyl group and desirably a (meth)acryloxypropyl group; n is an integer; each a is

independently 0, 1 or 2; each b is independently 0, 1 or 2; and a+b is 1 or 2.

[36] The number of repeating units in the silicon polymer component endcapped with at least one (meth)acrylate group may be varied to achieve specific molecular weights, viscosities and other chemical or physical properties. Generally n is an integer such that the viscosity is from about 25 cps to about 2,500,000 cps at 25° C., such as when n is from 1 to 1,200 and desirably from 10 to 1,000. The silicon polymer component endcapped with at least one (meth)acrylate group may be present in amounts sufficient to provide enhanced photocuring and addition curing capability. Desirably this component is included in amounts of about 10 to about 40% by weight and more desirably about 20 to 30% by weight of part B.

[37] A particularly desirable (meth)acrylate group comprising silicone has the following formula IV:



IV

wherein MA is a (meth)acrylate or (meth)acryloxyalkyl group such as a(meth)acryloxypropyl group; R1 and R2 are as defined in Structure III above; and c is 0 or 1.

[38] Part A and part B may be present in the ratio of part A to part B from about 1:10 to about 10:1, desirably about 1:5 to about 5:1, and more desirably in a ratio of about 1:1.

[39] The viscosity of the composition when parts A and part B are combined is desirably in the range of about 100 to 100,000 cps(mPas), more desirably on the range of about 500 to about 50,000, and even and more desirably in the range of about 500 cps to about 5,000 cps.

[40] The hardness of the cured compositions can be tailored for particular applications and for desired properties. Generally hardness may range from a shore hardness scale 00 of about 10 to about 30 (after photocure), to about 20 to about 70 (after 48 hour room temperature addition cure).

[41] The compositions of the present invention provide relatively fast curing (60 seconds or less) initially due to photocuring, followed by room temperature (RT) hydrosilylation addition cure.

[42] These advantages, as well as others, are obtained, while also providing a stable formulation.

EXAMPLES

Examples 1-3:

Light and addition cure silicone optical clear adhesive formulations

[43] Example 1-3 are two part light and addition-curable LOCA formulations. Part A contains vinyl terminated polydimethysiloxane (PDMS) and a platinum catalyst, Part B contains vinyl terminated polydimethysiloxane (PDMS), acrylate-terminated PDMS (acrylic end capped silanol terminated polydimethylsiloxane prepared as described in Example 3 of U.S. Pat. No. 5,663,269), organohydropolysiloxane, plasticizer, and photoinitators (from BASF). The sample formulations are captured below in Table 1, 2, 3.

Table 1

Example 1	Part A	Part B
Component	Wt%	Wt%
Vinyl terminated polydimethysiloxane (Evonik Polymer 1000	99.95	14.8
Vinyl Silicone (Evonik Polymer MV 2000)		50
Organohydropolysiloxane, (Evonik Crosslinker 110)		5
Acrylate terminated polydimethylsiloxane (viscosity 1,200 mPas)		30

Table 1		
Example 1	Part A	Part B
Component	Wt%	Wt%
Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene(Pt about 2%)	0.05	
Irgacure 1173 (Photoinitiator)		0.1
Irgacure TPO (Photoinitiator)		0.1
total	100	100

Table 2		
Example 2	Part A	Part B
Component	wt%	wt%
Vinyl terminated polydimethysiloxane Evonik Polymer VS 1000	70	0
Vinyl terminated polydimethysiloxane Evonik Polymer VS 200	29.95	0
PDMS fluid Dow Corning 200® Fluid 100cs	0	10
Organohydropolysiloxane, Evonik Modifier 705)	0	34.66
Organohydropolysiloxane, Evonik Crosslinker 110	0	5
acrylate terminated polydimethylsiloxane (viscosity 1,200 mPas)	0	50
Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene(Pt about 2%)	0.05	0
Irgacure 1173 (Photoinitiator)	0	0.15
Irgacure TPO (Photoinitiator)	0	0.15
total	100	100

Table 3		
Example 3	Part A	Part B
Component	wt%	wt%
Vinyl terminated polydimethysiloxane Evonik Polymer VS 1000	99.935	0
Organohydropolysiloxane, Evonik Modifier 705	0	47.2
Organohydropolysiloxane, Evonik Crosslinker 110	0	2.5
acrylate terminated polydimethylsiloxane (viscosity 1,200 mPas)	0	50
Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene(Pt about 2%)complex)	0.065	0
Irgacure 1173 (Photoinitiator)	0	0.15
Irgacure TPO (Photoinitiator)	0	0.15
total	100	100

Example 4:

Comparative Example 4: one-component light and moisture curable silicone LOCA formulation

[44] Comparative Example 4 is a one component (1K) light and moisture-curable LOCA formulation. This example uses vinyltrimethoxy silane as a moisture scavenger and dimethyltin dineodecanoate as a moisture catalyst. The Comparative Example 4 formulation is captured below in Table 4.

Table 4	
Comparative Example 4	
Component	Wt%
Acrylate terminated polydimethylsiloxane (viscosity 1,200 mPas)	98.75
Vinyl trimethoxysilane (VTMO)	1
Irgacure 1173 (Photoinitiator)	0.1
Irgacure TPO (Photoinitiator)	0.1
Tin Catalyst dimethyltin dineodecanoate	0.05
total	100

Example 5:

Performance Evaluation

[45] The evaluation methods for the adhesive compositions of Examples are as follows:

[46] For Examples 1-3, part A and Part B were mixed in 1:1 volume ratio. After mixing, photocuring was conducted using a mercury arc lamp that emits UV radiation of at least about 3000 mW/cm^2. Addition curing was conducted at a temperature of about 23°C. UV and addition dual curing was employed first by exposure to the mercury arc lamp and then by placement at room temperature for a defined period of time. Addition curing speed is measured by gel time when the mixed material is not movable anymore by a spatula. Shore 00 hardness was measured according to ASTM D2240.

[47] For Comparative Example 4, Moisture curing was conducted in a humidity chamber at a temperature of about 23°C and a relative

humidity of about 50%. UV and moisture dual curing was employed first by exposure to the mercury arc lamp and then by placement in the humidity chamber with 23°C and 50% humidity for a defined period of time. Moisture curing speed is measured by gel time when the material is not movable anymore by a spatula. Shore 00 hardness was measured according to ASTM D2240.

[48] Laminated samples for optical property and lamination tests were prepared as following: Between two glass slides with a lamination thickness (or gap) of 12.5 mil (about 318 μm) was disposed the LOCA and curing by exposure to UV light was conducted as described previously. Laminated assemblies were formed as a result and were then exposed to elevated temperature conditions of about 95°C and QUV (QUV Accelerated Weathering Tester) (0.68W/m^2 @340nm, 50°C) for a period of time of about 500 hours. Under these aging conditions, defects at the bond line may develop, and if so observed and recorded. Performance test results summarized below in Table 5:

Table 5

Physical Property Evaluation		**Sample Nos.**			
		Example 1	**Example 2**	**Example 3**	**Comp. Example 4**
Light cure gel time		10 seconds	10 seconds	10 seconds	10 seconds
*Secondary cure Gel time		60 min	50min	4 hour	24 hour
Shore 00 hardness	UV cure	5	10	18	20
	Secondary cure	40	25	25	25
	UV+	50	55	65	50

Table 5					
Physical Property Evaluation		**Sample Nos.**			
		Example 1	**Example 2**	**Example 3**	**Comp. Example 4**
	secondary cure				
500 hour resistance test	95°C	No defect			
	QUV	No defect			

*Secondary cure for Examples 1-3 is addition cure

[49] All inventive compositions gel in less than 10 seconds under light exposure. However, the secondary addition cure of the inventive compositions was much faster than one-component moisture curing compositions. The cured properties are excellent for LOCA applications.

Example 6:

Dual Curing optical clear adhesive optical properties (Inventive using light and addition cure; comparative using UV and moisture cure)

[50] Optical properties and reliability tests of Example 2-3 and comparative example were evaluated and the results are captured below in Table 6. Samples for optical property measurements were made by preparing a two glass slide assembly with a thickness (or gap) of 12.5 mil (about 318 μm) therebetween. The samples were cured by UV only, secondary (addition cure or moisture cure) only or by UV and secondary

dual cure, as described previously. Optical properties -- typically transmittance, haze and the b* value (yellowness) -- were measured by a Datacolor 650 apparatus available from Datacolor Corporation, in compliance with ASTM D1003. The samples were also subjected to reliability test conditions, which are as follows: the cured samples were put in high temperature and high humidity chamber (about 85°C, 85% relative humidity), high temperature (about 95°C) and QUV **under the** 1000 hours. Optical properties of samples under 85 °C /85% RH were measured after letting samples dry at room temperature for >24hrs to remove moisture trapped in the samples.

Table 6

Aging time (hours)	**Aging condition**	**Optical properties**			
		Example 3		**Comparative Example 4**	
		Haze %	**Yellowness**	**Haze %**	**Yellowness**
0	Before aging	0.1	0	0	0.21
1000	85°C/85% RH	0.3	0.4	2.0	0.17
	95°C	0.2	0.25	0.2	0.11
	QUV	0.2	0.36	0.3	0.14

[51] Desirably, both haze and yellowness values are under 1.0 and thus considered sufficiently optically clear for purposes of the present invention. Two-parts light and addition cure

compositions have both haze and yellowness under 1.0 after 1000 hrs. reliability tests under all three conditions. Comparative example with light and moisture cure have haze value great than 1.0 after 1000hr exposure under 85 °C /85% RH.

Example 7:

[52] Inventive Composition I, from Example 1, was tested for shelf-life stability using accelerated aging tests at 50°C. Each of Part A and Part B samples were individually stored in a 50°C oven and the gel time of the two parts with respect to addition cure was tested. The results are provided in Table 7.

Table 7

Accelerated aging time	**Gel time**
0 day	60 min
4 weeks	50 min

What is Claimed is:

1. A two part, dual curing adhesive composition comprising:

A. a first part comprising:

1) one or more vinyl silicone-based polymer(s)

2) a platinum catalyst;

B. a second part comprising:

1) optionally one or more vinyl silicone-based polymer(s)

2) a silicone hydride cross-linker; and

3) one or more (meth)acrylate end-capped silicone polymer(s);

wherein at least one of part A and part B includes at least one photoinitiator.

2. The two part adhesive composition of claim 1, wherein the dual curing mechanisms consist of radiation cure and hydrosilylation addition-cure

3. The two part adhesive composition of claim 1, wherein the ratio of part A to part B is from about 1:10 to about 10:1.

4. The two part adhesive composition of claim 1, wherein the one or more vinyl polymer(s) of part A is included in amounts of about 40% to about 90% by weight of part A.

5. The two part adhesive composition of claim 1, wherein the platinum catalyst is present in amounts of about 0.01% to about 2.0% by weight of Part A.

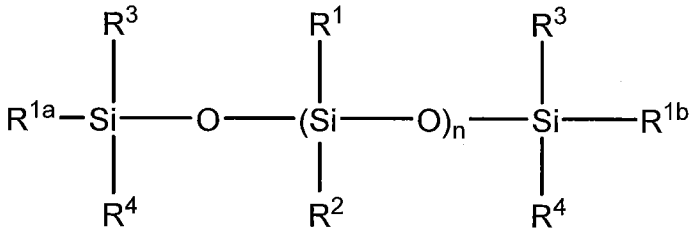
6. The two part adhesive composition of claim 1, wherein the one or more (meth)acrylate end-capped silicone polymer(s) is present in amounts of about 10% to about 40% by weight of part B.

7. The two part adhesive composition of claim 1, wherein the photoinitiator is present in amounts of about 0.02% to about 0.50%.

8. The two part adhesive composition of claim 1, wherein the optional vinyl silicone-based polymer(s) of part B are present in amounts of about 40% to about 90%.

9. The two part adhesive composition of claim 1, wherein the platinum catalyst comprises a platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex.

10. The two part adhesive composition of claim 1, wherein the one or more vinyl silicone-based polymer(s)of part A has the structure:

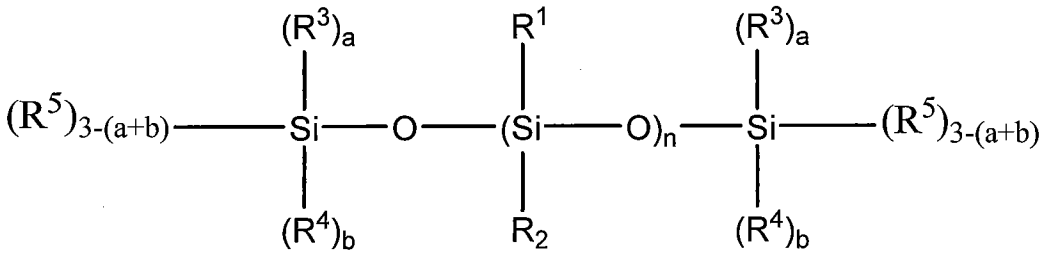


I

wherein where R^{1a} ,R^{1b},R1, R^2, R^3 and R^4 are each independently selected from alkyl, alkoxy, alkenyloxy,

aryloxy, aryl, methacryl, methacryloxy and combinations thereof, provided that at least one of R^{1a} and R^{1b} must be a vinyl group; and n is between 100 and 1,200.

11. The two part adhesive composition of claim 1, wherein the one or more (meth)acrylate end-capped silicone polymer(s)has the structure:



III

wherein R^1, R^2, R^3 and R^4 may be the same or different and are monovalent hydrocarbon radicals having up to 10 carbon atoms (C_{1-10}) or halo or cyano substituted hydrocarbon radicals; R^3 may also be a monovalent heterohydrocarbon radical having up to 10 carbon atoms (C_{1-10}) where the hereto atoms are selected from halo atoms, O, N, and S; R^5 is alkoxy (C_{1-10}), such as methyloxy, ethyloxy, isopropoxy or (meth)acryloxypropyl group; n is an integer; each a is independently 0, 1 or 2; each b is independently 0, 1 or 2; and a+b is 1 or 2.

12. The two part adhesive composition of claim 11, wherein the methacrylate end-capped silicone includes methacryloxypropyltrimethoxysilane.

13. The two part adhesive composition of claim 1, the one or more vinyl silicone-based polymer(s) includes a monofuntional vinyl silicone.

14. The two part adhesive composition of claim 1, further comprising a component selected from the group consisting of diluents, thickeners, stabilizers, colorants, pigments, antioxidants, plasticizers, rheology modifiers and combinations thereof.

15. Cured reaction products of the two part adhesive composition of claim 1 being an optically clear product having a haze value of 0 to about 0.04%.

16. Cured reaction products of the two part adhesive composition of claim 1 being an optically clear product having a Shore 00 hardness of about 40 to about 50.

17. A process for making an assembly comprising the steps of:

providing a display panel and a top substrate comprising a cover lens or a touch panel;

providing the two part adhesive composition according to claim 1;

mixing the two parts of the adhesive composition;

disposing the mixed adhesive composition between the top substrate and the display panel; and

curing the adhesive composition by exposure to radiation in the electromagnetic spectrum and further permitting any uncured

adhesive composition to cure at room temperature through hydrosilylation addition-cure.

18. An assembly comprising a display panel, a top substrate for the display panel and a reaction product of the adhesive composition of claim 1 disposed therebetween.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/054181

A. CLASSIFICATION OF SUBJECT MATTER
IPC (2019.01) C09J 143/04, C08G 77/12, C08G 77/14, C08G 77/20, C08L 83/04, C08J 3/24, B32B 37/12

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)
IPC (2019.01) C09J, B32B

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)
Databases consulted: Esp@cenet, Google Patents, Google Scholar, Orbit
Search terms used: Adhesive; two parts, dual cure , radiation, hydrosilylation, polysiloxanes, LOCA, acrylate, vinyl, touch panel; platinum

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4585669 A ECKBERG R. P. 29 Apr 1986 (1986/04/29) The whole document	1-18
A	US 4587137 A ECKBERG R. P 06 May 1986 (1986/05/06) Abstract	1-18
A	US 2004116547 A1 BENNINGTON L. D. 17 Jun 2004 (2004/06/17) abstract	1-18
A	US 4603168 A SASAKI S. et al. 29 Jul 1986 (1986/07/29) abstract	1-18
A	US 6376569 B1 OXMAN J. D. et al. 23 Apr 2002 (2002/04/23) abtsract	1-18

[X] Further documents are listed in the continuation of Box C. [X] 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 application or patent 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
24 Jan 2019	27 Jan 2019
Name and mailing address of the ISA: Israel Patent Office Technology Park, Bldg.5, Malcha, Jerusalem, 9695101, Israel Facsimile No. 972-2-5651616	Authorized officer GUTMAN Ariel Telephone No. 972-2-5657816

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/054181

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 8642674 B2 SHIN-ESTU CHEMICAL CO. LTD. 04 Feb 2014 (2014/02/04) abstract	1-18

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US2018/054181

Patent document cited search report	Publication date	Patent family member(s)	Publication Date
US 4585669 A	29 Apr 1986	US 4585669 A	29 Apr 1986
		CA 1256239 A	20 Jun 1989
		JP S6189256 A	07 May 1986
		JP H0129511 B2	12 Jun 1989
US 4587137 A	06 May 1986	US 4587137 A	06 May 1986
		CA 1256240 A	20 Jun 1989
		JP S6195069 A	13 May 1986
		JP H0655889 B2	27 Jul 1994
US 2004116547 A1	17 Jun 2004	US 2004116547 A1	17 Jun 2004
		AU 9212198 A	08 Mar 1999
		AU 737212 B2	09 Aug 2001
		BR 9811313 A	29 Aug 2000
		CA 2302685 A1	25 Feb 1999
		CN 1270614 A	18 Oct 2000
		EP 1005510 A1	07 Jun 2000
		JP 2001515117 A	18 Sep 2001
		KR 20010023087 A	26 Mar 2001
		WO 9909103 A1	25 Feb 1999
US 4603168 A	29 Jul 1986	US 4603168 A	29 Jul 1986
		CA 1285672 C	02 Jul 1991
		DE 3585041 D1	13 Feb 1992
		EP 0153700 A2	04 Sep 1985
		EP 0153700 A3	26 Aug 1987
		EP 0153700 B1	02 Jan 1992
		JP S60177029 A	11 Sep 1985
		JP H041769 B2	14 Jan 1992
US 6376569 B1	23 Apr 2002	US 6376569 B1	23 Apr 2002

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US2018/054181

Patent document cited search report	Publication date	Patent family member(s)	Publication Date
		CA 2096228 A1	14 Jun 1992
		DE 69122625 D1	14 Nov 1996
		DE 69122625 T2	17 Apr 1997
		EP 0561893 A1	29 Sep 1993
		EP 0561893 B1	09 Oct 1996
		JP H06503591 A	21 Apr 1994
		WO 9210543 A1	25 Jun 1992
US 8642674 B2	04 Feb 2014	US 2013096223 A1	18 Apr 2013
		US 8642674 B2	04 Feb 2014
		EP 2584003 A1	24 Apr 2013
		JP 2013087199 A	13 May 2013