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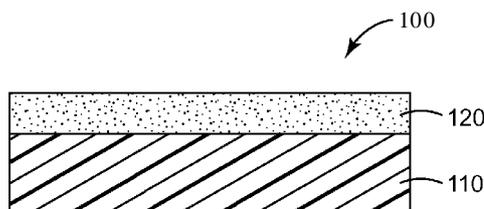


FIG. 1

(57) Abstract: Dual condensation cure silicone systems are described. Such systems include hydroxyl-functional(s), hydride-functional silane(s), platinum catalyst(s) and Ti(IV) complex(es). Systems including alkoxy-functional crosslinker(s) are also described. Articles, including adhesive articles included the cured reaction product of such dual condensation cure silicone systems are also described.



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DUAL CONDENSATION CURE SILICONEFIELD

[0001] The present disclosure relates to condensation cure silicone systems. Specifically, to dual condensation cure silicone systems including both a platinum catalyst and a titanate ester. Methods of curing, cured compositions, and articles incorporating cured compositions are also described.

SUMMARY

[0002] Briefly, in one aspect, the present disclosure provides a dual cure silicone system comprising a silanol-functional polyorganosiloxane, a hydride-functional silane, a platinum catalyst, and a Ti(IV) complex. In some embodiments, the system comprises two or more different silanol-functional polyorganosiloxanes. In some embodiments, the system further comprises an alkoxy-functional silane crosslinker. In some embodiments, the alkoxy-functional silane crosslinker is selected from the group consisting of divinyl-diethoxysilane, triethoxysilane, tetraethoxysilane, bis(triethoxysilyl)ethane, and combinations thereof.

[0003] In some embodiments, the platinum catalyst comprises at least one of a Pt(0) complex, a Pt(II) complex, and a Pt(IV) complex, e.g., bis(1,3-divinyl-1,1,3,3-tetramethyldisiloxane) platinum(O). In some embodiments, the Ti(IV) complex is selected from the group consisting of titanium(IV) 2-ethylhexoxide, titanium di-n-butoxide(bis-2,4-pentanedionate), titanium(IV) isopropoxide, titanium(IV) n-butoxide, titanium(IV) nethoxide, titanium(IV) diisopropoxide bis(ethylacetoacetate), titanium(IV) diisopropoxide (bis-2,4-pentanedionate), and combinations thereof.

[0004] In another aspect, the present disclosure provides an article comprising a crosslinked silicone layer comprising the reaction product of a dual cure silicone system of the present disclosure. In some embodiments, the article further comprises a substrate, wherein the crosslinked silicone layer covers at least a portion of a first surface of the substrate. In some embodiments, the article further comprises an adhesive layer, wherein the adhesive layer covers at least a portion of the crosslinked silicone layer.

[0005] The above summary of the present disclosure is not intended to describe each embodiment of the present invention. The details of one or more embodiments of the invention are also set forth in the description below. Other features, objects, and advantages of the invention will be apparent from the description and from the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] **FIG. 1** illustrates an exemplary release article according to some embodiments of the present disclosure.

[0007] FIG.2 illustrates an exemplary adhesive article according to some embodiments of the present disclosure.

### DETAILED DESCRIPTION

[0008] Curable silicone materials are useful in a variety of applications. For example, some curable silicone systems can be used to prepare release materials, e.g., release coatings for adhesives including, e.g., pressure sensitive adhesives. Silicone systems have been prepared using a variety of approaches, including addition-cure and condensation-cure chemistries.

[0009] Addition-cure refers to a system where curing is achieved through the addition of Si-H across a pi ( $\pi$ ) bond, i.e., hydrosilation. One advantage of addition-cure systems is that precious metal catalysts (e.g., platinum catalysts) are exceptionally efficient, e.g., even with low parts per million (ppm) of platinum, the hydrosilylation reaction can occur rapidly without producing by-products. Both thermal-cure and radiation-cure, precious metal catalysts have been used in addition-cure (i.e., hydrosilation) silicone systems.

[0010] Condensation cure refers to a system where curing is achieved through the reaction of Si-OH and Si-H groups or Si-OH and Si-OH groups leading to the formation of Si-O-Si linkages and hydrogen gas or water. Exemplary condensation-cure silicone systems include those comprising hydroxyl-functional polyorganosiloxane(s) and hydride-functional silane(s). Typically, condensation-cure silicone systems have been cured with tin catalysts. Tin-based catalysts catalyze two major reactions, i.e., chain-extension reactions involving two silanol groups, and cross-linking or curing reactions involving a silanol group and a silicon hydride group.

[0011] In co-filed U.S. Patent Application No. 61/578,039 (Rathore et al., "Platinum-Catalyzed Condensation-Cure Silicone Systems," filed December 20, 2011), the discovery that platinum catalysts could be used in condensation-cure silicone systems was described. Co-filed U.S. Patent Application No. 61/578,031 (Rathore et al., "Photoactivated, Precious Metal Catalysts in Condensation-Cure Silicone Systems," filed December 20, 2011) describes the discovery that photoactivated precious metal catalysts, including platinum, can be used in condensation-cure silicone systems.

[0012] The present disclosure relates to the inventors surprising discovery that synergistic improvements in the cure of silicone systems could be achieved by combining a platinum-catalyzed silicone system with a titanium complex. In various embodiments, such "dual cure" silicone systems exhibit one or more of the following synergistic effects: (1) reduction in the amount of platinum catalyst, (2) reduction in the amount of silane cross-linker, (3) reduction in the cure temperature, and (4) improvement in control of the release of adhesives from the cured silicone compositions.

[0013] Generally, the platinum-catalyzed silicone systems comprise a condensation-cure silicone system and a catalyst comprising a platinum complex. In some embodiments, the silicone system comprises a hydroxyl-functional polyorganosiloxane and a hydride-functional silane. Generally, the

hydride-functional silane comprises at least two, and in some embodiments three or more silicon-bonded hydrogen atoms.

**[0014]** Generally, any known hydroxyl-functional polyorganosiloxane suitable for use in condensation-cure systems can be used in the compositions of the present disclosure, and such materials are well-known and readily obtainable. Exemplary polyorganosiloxanes include poly(dialkylsiloxane) (e.g., poly(dimethylsiloxane)), poly(diarylsiloxane) (e.g., poly(diphenylsiloxane)), poly(alkylarylsiloxane) (e.g., poly(methylphenylsiloxane)), poly(dialkylalkylarylsiloxane) (e.g., poly(dimethylmethylphenylsiloxane)), and poly(dialkyldiarylsiloxane) (e.g., poly(dimethyldiphenylsiloxane)). Both linear and branched polyorganosiloxanes may be used. In some embodiments, one or more of the organo groups may be halogenated, e.g., fluorinated.

**[0015]** Exemplary hydroxyl-functional polyorganosiloxanes include silanol-terminated polydimethylsiloxanes including, e.g., those available from Gelest, Inc., Morrisville, Pennsylvania, including those available under the trade names DMS-S12, -S14, -SI 5, -S21, -S27, -S31, -S32, -S33, -S35, -S42, -S45, and -S51; and those available from Dow Corning Corporation, Midland, Michigan, including those available under the trade names XIAMETER OHX Polymers and 3-0084 Polymer, 3-0113 Polymer, 3-0133 Polymer, 3-0134 Polymer, 3-0135 Polymer, 3-0213 Polymer, and 3-3602 Polymer.

**[0016]** Generally, any known hydride-functional silane suitable for use in condensation-cure systems can be used in the compositions of the present disclosure, and such materials are well-known and readily obtainable. Exemplary hydride-functional silanes include those available from Dow Corning Corporation, including those available under the trade name SYL-OFF (e.g., SYL-OFF 7016, 7028, 7048, 7137, 7138, 7367, 7678, 7689, and SL-series crosslinkers), and those available from Gelest, Inc.

**[0017]** Condensation cure silicone systems that contain both one or more silanol-terminated polyorganosiloxane(s) and one or more hydride-functional silane crosslinkers are also known. Examples of such systems include those available from Dow Corning Corporation, including those available under the trade names SYL-OFF (e.g., SYL-OFF 292 and SYL-OFF 294).

**[0018]** As is known by one of ordinary skill in the art, the relative amounts of the hydroxyl-functional polyorganosiloxane(s) and the hydride-functional silane(s) can be selected to obtain a variety of use compositions. Factors affecting such selections include the specific polyorganosiloxane(s) and silane(s) selected, the relative functionality of the silane(s) compared to the polyorganosiloxane(s), the desired degree of cross-linking and/or chain extension, and the desired final properties including, e.g., release force, mechanical properties, cure conditions, percent extractables, and the like. Generally, the relative amounts are selected such that ratio of molar equivalents of hydroxyl functionality to molar equivalents of hydride functionality is between 0.01 and 10, inclusive, e.g., between 0.04 and 2, inclusive.

**[0019]** Generally, the platinum-catalyzed silicone systems comprise a platinum complex, e.g., a Pt(0), Pt(II) or Pt(IV) complex.

[0020] In some embodiments, the compositions comprise at least one Pt(0) complex. In some embodiments, the Pt(0) complex is bis-(1,3-divinyl-1,1,3,3-tetrametyldisiloxane) platinum (0) (commonly known as Karstedt catalyst). Other exemplary Pt(0) complexes suitable for use in some embodiments include (2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane) platinum(O), ethylenebis(triphenylphosphine) platinum(0), bis(tri-*tert*-butylphosphine) platinum(O), and tetrakis(triphenylphosphine) platinum(O).

[0021] In some embodiments, the compositions comprise at least one Pt(II) complex. In some embodiments, the Pt(II) complex is dimethyl (1,5-cyclooctadiene)platinum(II). Other exemplary Pt(II) complexes suitable for use in some embodiments include  $\eta^2$ -dichlorobis(triethylphosphine) platinum(II), dichlorobis(ethylenediamine) platinum(II), dichloro(1,5-cyclooctadiene) platinum(II), platinum(II) chloride, platinum(II) bromide, platinum(II) iodide,  $\eta^2$ -platinum(II)diammine dichloride, dichloro(1,2-diaminocyclohexane) platinum(II), and ammonium tetrachloroplatinate(II).

[0022] In some embodiments, the compositions comprise at least one Pt(IV) complex. In some embodiments, the Pt(IV) complex is dihydrogen hexachloroplatinate (IV) hexahydrate. Other exemplary Pt(IV) complexes suitable for use in some embodiments include platinum(IV) oxide hydrate, and ammonium hexachloroplatinate(IV) .

[0023] Generally, the amount of platinum catalyst present will be at least 1 part per million (ppm) platinum based on the total weight of the hydroxyl-functional polyorganosiloxane and the hydride-functional silane, e.g., at least 5 ppm, or even at least 10 ppm. In some embodiments, the composition comprises 5 to 200 ppm platinum based on the total weight of the hydroxyl-functional polyorganosiloxane and the hydride-functional silane, e.g., 5 to 100 ppm, 10 to 100 ppm, or even 10 to 50 ppm.

[0024] The compositions of the present disclosure also include a Ti(IV) complex. Exemplary Ti(IV) complexes suitable as catalysts in various embodiments of the present disclosure include titanium(IV) 2-ethylhexoxide, titanium di-*n*-butoxide(bis-2,4-pentanedionate), titanium(IV) isopropoxide, titanium(IV) *n*-butoxide, titanium(IV) ethoxide, titanium(IV) diisopropoxide bis(ethylacetoacetate), and titanium(IV) diisopropoxide (bis-2,4-pentanedionate). In some embodiments, combinations of two or more titanium(IV) complexes may be used.

[0025] In some embodiments, the compositions of the present disclosure include at least 3 wt.%, e.g., at least 5 wt.% or even at least 8 wt.% of the Ti(IV) complex(es), based on the total weight of solids in the composition. In some embodiments, the compositions of the present disclosure include no greater than 30 wt.%, e.g., no greater than 20 wt.%, or even no greater than 15 wt.%, of the Ti(IV) complex(es), based on the total weight of solids in the composition. In some embodiments, the compositions of the present disclosure include 3 to 30 wt.%, e.g., 5 to 20 wt.%, or even 8 to 15 wt.% of the Ti(IV) complex(es), based on the total weight of solids in the composition.

[0026] In some embodiments, the compositions of the present disclosure also include one or more alkoxy-functional silane crosslinkers. Any known alkoxy-functional silane crosslinker may be used. Generally, such crosslinkers include at least two, and preferably three or more, alkoxy-functional groups. Exemplary alkoxy-functional silane crosslinkers suitable for use in various embodiments of the present disclosure include divmyldiethoxysilane, triethoxysilane, tetraethoxysilane, and bis(triethoxysilyl)ethane (alternatively known as hexaethoxydisilethylene). In some embodiments, combinations of two or more alkoxy-functional silane crosslinkers may be used.

[0027] In some embodiments, the compositions of the present disclosure include at least 3 wt.%, e.g., at least 5 wt.% or even at least 8 wt.% of the alkoxy-functional silane(s), based on the total weight of solids in the composition. In some embodiments, the compositions of the present disclosure include no greater than 30 wt.%, e.g., no greater than 20 wt.%, or even no greater than 15 wt.%, of the alkoxy-functional silane(s), based on the total weight of solids in the composition. In some embodiments, the compositions of the present disclosure include 3 to 30 wt.%, e.g., 5 to 20 wt.%, or even 8 to 15 wt.% of the alkoxy-functional silane(s), based on the total weight of solids in the composition.

[0028] When cured, the dual condensation cure systems of the present disclosure may be suitable for a wide variety of applications. In some embodiments, the cured compositions may be suitable as release layers for release liners. In some embodiments, such liners may be suitable for use with an adhesive article.

[0029] An exemplary release article **100** according to some embodiments of the present disclosure is illustrated in **FIG. 1**. Release article **100** includes release layer **120** and substrate **110**. In some embodiments, release layer **120** is directly bonded to substrate **110**. In some embodiments, one or more layers, e.g., primer layers, may be located between release layer **120** and substrate **110**. Any known material may be suitable for use in substrate **110** including paper and polymeric films. Any of the compositions of the present disclosure may be coated on such substrates and cured to provide the release layer. Conventional coating and curing methods are well known, and one of ordinary skill in the art may select those appropriate for the selected condensation-cure composition and substrate selected.

[0030] An exemplary adhesive article **200** incorporating release article **100** is shown in **FIG 2**. Adhesive layer **130** is in direct contact with the surface of release layer **120**, opposite substrate **110**. Generally, any known adhesive may be used and one of ordinary skill in the art can select an adhesive appropriate for the selected release layer. In some embodiments, acrylic adhesives may be used. In some embodiments, adhesive article **200** may also include optional layer **140**, which may be adhered directly to adhesive layer **130**, opposite release layer **120**. In some embodiments, one or more intervening layers, e.g., primer layers, may be present between adhesive layer **130** and optional layer **140**. Optional layer **140** may be any of a wide variety of known materials including paper, polymeric film, foam, woven and nonwoven webs, scrims, foils (e.g., metal foils), laminates, and combinations thereof.

[0031] Examples.

[0032] Unless otherwise noted, all parts, percentages, ratios, etc., in the examples and in the remainder of the specification are by weight. Unless otherwise noted, all chemicals were obtained from, or are available from, chemical suppliers such as Sigma-Aldrich Chemical Company, St. Louis, Missouri.

[0033] "Silicone-A" is a 30 weight percent solids dispersion of a blend of reactive hydroxysilyl-functional siloxane polymer(s) (said to comprise hydroxyl-terminated polydimethylsiloxane) and hydrosilyl-functional polysiloxane crosslinker (said to comprise polymethylhydrogensiloxane) in xylene (a composition obtained from Dow Corning Corporation, Midland, Michigan, under the trade designation SYL-OFF 292).

[0034] "Pt-Cat" was bis(1,3-divinyl-1,1,3,3-tetrametyldisiloxane) platinum(O) (also known as Karstedt catalyst, 2 wt% platinum in xylene) purchased from Sigma-Aldrich Chemical Company, and kept in the dark before use.

[0035] "Ti-Cat" was titanium (IV)-2-ethylhexoxide (alternatively known as tetraoctyltitanate), and was obtained from Gelest, Inc., Morrisville, PA.

[0036] "XL-1" was bis(triethoxysilyl)ethane (alternatively known as hexaethoxydisilethylene), and was obtained from Gelest, Inc., Morrisville, PA, under trade designation SIB1817.0.

[0037] "XL-2" was tetraethoxysilane, obtained from Gelest, Inc.

[0038] "XL-3" was divinyl-diethoxysilane obtained from Gelest, Inc.

[0039] "XL-4" was triethoxysilane, obtained from Gelest, Inc.

[0040] Heptane and diallyl maleate were purchased from Sigma-Aldrich Chemical Company, St. Louis, MO, and were used as received.

[0041] Silicone Coat Weight Procedure. Silicone coat weights were determined by comparing approximately 3.69 centimeter diameter samples of coated and uncoated substrates using an EDXRF spectrophotometer (obtained from Oxford Instruments, Elk Grove Village, IL under trade designation OXFORD LAB X3000).

[0042] Silicone Extractables Procedure. Unreacted silicone extractables were measured on cured thin film formulations to ascertain the extent of silicone crosslinking immediately after the coatings were cured. The percent extractable silicone, (i.e., the unreacted silicone extractables), a measure of the extent of silicone cure on a release liner, was measured by the following method.

[0043] The silicone coat weight of a 3.69 centimeter diameter sample of coated substrate was determined according to the Silicone Coat Weight Procedure. The coated substrate sample was then immersed in and shaken with methyl isobutyl ketone (MIBK) for 5 minutes, removed, and allowed to dry. The silicone coating weight was measured again according to the Silicone Coat Weight Procedure.

Silicone extractables were attributed to the weight difference between the silicone coat weight before and after extraction with MIBK as a percent using the following formula:

$$(a - b) / a * 100 = \text{Percent Extractable Silicone}$$

wherein a = initial coating weight (before extraction with MIBK); and

wherein b = final coating weight (after extraction with MIBK).

**[0044]** Release Liner Adhesion Procedure. The 180° angle peel adhesion strength of a release liner to an adhesive sample was measured in the following manner, which is generally in accordance with the test method described in Pressure Sensitive Tape Council PSTC-101 method D (Rev 05/07) "Peel Adhesion of Pressure Sensitive Tape."

**[0045]** The example and comparative example release liners prepared as described below were coated with an acrylic radiation-sensitive syrup (90 parts by weight isooctyl acrylate and 10 parts by weight acrylic acid) with a notched bar coater to form a continuous coating of acrylic syrup nominally 50 micrometers thick. The resulting "wet" coating was then polymerized to more than 95 % conversion by exposing the acrylic syrup to UV-A irradiation from 20W 350BL lamps (available from Osram Sylvania, Danvers, MA) in a nitrogen-inerted environment. Upon curing, the polymerized syrup formed a pressure-sensitive adhesive (PSA) transfer tape on the release liner. The resulting adhesive transfer tape was aged for 7 days prior to testing for release liner adhesion.

**[0046]** After aging, a 2.54 centimeter wide and approximately 20 centimeter in length sample of the adhesive transfer tape was cut using a specimen razor cutter. The cut sample was applied with its exposed adhesive side down and lengthwise onto the platen surface of a peel adhesion tester (Slip/Peel Tester, Model 3M90, obtained from Instrumentors, Incorporated, Strongsville, Ohio). The applied sample was rubbed down on the test panel using light thumb pressure. The adhesive transfer tape on the platen surface was then rolled twice with a 2 kilograms rubber roller at a rate of 61 centimeter/minute.

**[0047]** The release liner was carefully lifted away from the adhesive transfer tape on the platen surface, doubled-back at an angle of 180 degrees, and secured to clamp of the peel adhesion tester. The 180 degree angle release liner peel adhesion strength was then measured at a peel rate of 38.1 millimeters/second. A minimum of two test specimens were evaluated with results obtained in gram/inch which were used to calculate the average peel force. This average value was then converted to Newtons per meter (N/m). All release tests were carried out in a facility at constant temperature (23 °C) and constant relative humidity (50 percent).

**[0048]** Example 1 (EX-1) was prepared by first diluting Silicone-A (6.88 grams) with heptane (12.80 grams) followed by addition of diallyl maleate (0.15 gram) and Pt-Cat (150 parts per million of Pt(0)). Then, XLINK-1 and Ti-Cat were added to the aforementioned mixture, each at 10 wt.% with respect to total amount of solids in the final formulation. The formulation was thoroughly mixed and coated on a 58#, corona-treated, polyethylene-coated kraft paper ("PCK", obtained from Jen-Coat, Inc., Westfield,

MA) with a # 3 Mayer bar. The coated layer was cured at 110 °C for 60 seconds in an oven equipped with solvent exhaust. The (%) silicone extractables and release liner adhesion were determined using the procedures described above.

[0049] Comparative Examples 1-3 (CE-1 through CE-3).

[0050] CE-1 was prepared in the same manner as EX-1, except that the formulation did not contain any diallyl maleate or Pt-Cat. CE-2 was prepared in the same manner as EX-1, except that the formulation did not contain any crosslinker (XLINK) or Ti-Cat. CE-3 was prepared in the same manner as CE-2, except that the amount of Pt-Cat was 100 parts per million of Pt(0). The formulations of CE-1 through CE-3 were each thoroughly mixed and coated on PCK with a # 3 Mayer bar. The coated layers were cured at 110 °C for 60 seconds in an oven equipped with solvent exhaust. The (%) silicone extractables and release liner adhesion were determined using the procedures described above.

[0051] Examples 2-5 (EX-2 through EX-5).

[0052] EX-2 through EX-5 were prepared in the same manner as EX-1 and each formulation contained Silicone-A (6.88 grams) diluted with heptane (12.80 grams), diallyl maleate (0.15 gram), Pt-Cat (100 parts per million of Pt(0)), Ti-Cat (10 wt % with respect to the total amount of solids in the final formulation), and a crosslinker (10 wt% with respect to the total amount of solids in the final formulation). The crosslinkers for EX-2 through EX-5 were XLINK-1, XLINK-2, XLINK-3, and XLINK-4, respectively. Formulations EX-2 through EX-5 were each thoroughly mixed and coated on PCK with a # 3 Mayer bar. The coated layers were cured at 110 °C for 60 seconds in an oven equipped with solvent exhaust. The (%) silicone extractables and release liner adhesion were determined using the procedures described above.

[0053] Table 1 below summarizes the compositions of the examples and comparative examples. The silicone extractables and release liner adhesion results are summarized in Table 2.

Table 1: Sample compositions.

	EX-1	CE-1	CE-2	CE-3	EX-2	EX-3	EX-4	EX-5
Silicone-A (g)	6.88	6.88	6.88	6.88	6.88	6.88	6.88	6.88
crosslinker type	XL-1	XL-1	none	none	XL -1	XL -2	XL -3	XL -4
(wt.%)	10	10	10	10	10	10	10	10
Pt-Cat (ppm)	150	none	150	100	100	100	100	100
Ti-Cat (wt.%)	10	10	none	none	10	10	10	10
Heptane (g)	12.80	12.80	12.80	12.80	12.80	12.80	12.80	12.80
Diallyl maleate (g)	0.15	none	0.15	0.15	0.15	0.15	0.15	0.15

Table 2: Test results.

	EX-1	CE-1	CE-2	CE-3	EX-2	EX-3	EX-4	EX-5
Extractables (wt.%)	4.9	60.0	24.3	30.7	8.6	15.0	6.0	4.0
Release (N/m)	18.3	*	30.1	28.0	18.5	18.0	18.3	18.0

\* Not measured.

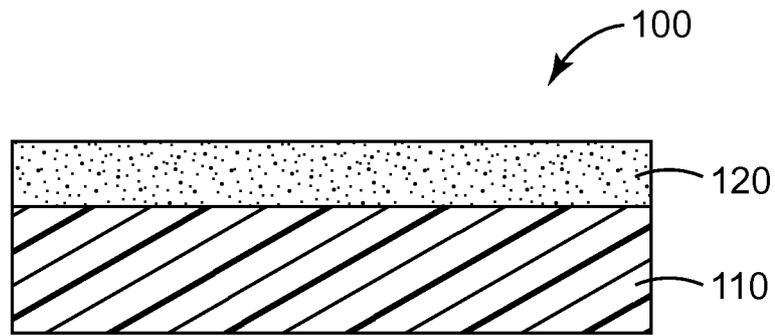
**[0054]** The Silicone Extractables Procedure was used as a measure of the extent of silicone cure on a release liner. The Release Liner Adhesion Procedure was used to measure the effectiveness of release liners prepared using the compositions according to the examples and comparative examples. The release value is a quantitative measure of the force required to remove a flexible adhesive from the release liner at a specific angle and rate of removal.

**[0055]** Comparing EX- 1 to CE- 1 and CE-2, it is clear that the dual cure system of EX- 1 yielded significant improvements in cure (lower percent extractables) and lower release values as compared to single cure systems such as CE-1 (platinum-only) and CE-2 (titanium-only). Comparing EX-2 through EX-5 to CE- 1 and CE-2, it is apparent that the dual-cure systems resulted in better performance over a range of crosslinker types and at lower levels of platinum catalyst (150 ppm for CE-2, and only 100 ppm for EX-2 through EX-5).

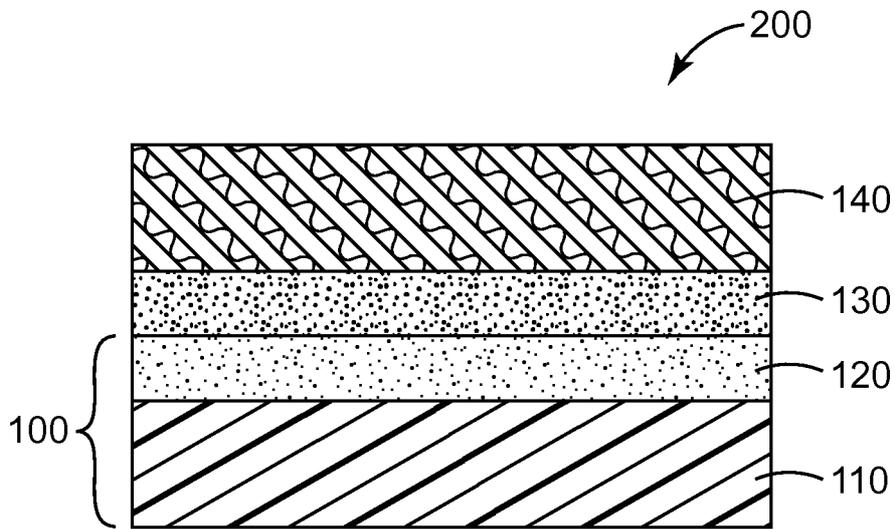
**[0056]** Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention.

What is Claimed is:

1. A dual cure silicone system comprising a silanol-functional polyorganosiloxane, a hydride-functional silane, a platinum catalyst, and a Ti(IV) complex.
2. The dual cure silicone system of claim 1, further comprising an alkoxy-functional silane crosslinker.
3. The dual cure silicone system of claim 2, wherein the alkoxy-functional silane crosslinker is selected from the group consisting of divinyl-diethoxysilane, triethoxysilane, tetraethoxysilane, bis(triethoxysilyl)ethane, and combinations thereof.
4. The dual cure silicone system according to any one of the preceding claims, wherein the platinum catalyst comprises at least one of a Pt(0) complex, a Pt(II) complex, and a Pt(IV) complex.
5. The dual cure silicone system of claim 4, wherein the platinum catalyst comprises at least one Pt(0) complex.
6. The dual cure silicone system of claim 5, wherein the platinum catalyst comprises bis(1,3-divinyl-1,1,3,3-tetramethyldisiloxane) platinum(0).
7. The dual cure silicone system according to any one of the preceding claims, wherein the Ti(IV) complex is selected from the group consisting of titanium(IV) 2-ethylhexoxide, titanium *di-n*-butoxide(bis-2,4-pentanedionate), titanium(IV) isopropoxide, titanium(IV) *n*-butoxide, titanium(IV) ethoxide, titanium(IV) diisopropoxide bis(ethylacetoacetate), titanium(IV) diisopropoxide (bis-2,4-pentanedionate), and combinations thereof.
8. The dual cure silicone system of claim 7, wherein the Ti(IV) complex comprises titanium (IV)-2-ethylhexoxide.
9. The dual cure silicone system according to any one of the preceding claims, wherein the system comprises two or more different silanol-functional polyorganosiloxanes.
10. An article comprising a crosslinked silicone layer comprising the reaction product of the dual cure silicone system according to any one of the preceding claims.
11. The article of claim 10, further comprising a substrate, wherein the crosslinked silicone layer covers at least a portion of a first surface of the substrate.
12. The article of claim 11, further comprising an adhesive layer, wherein the adhesive layer covers at least a portion of the crosslinked silicone layer.



**FIG. 1**



**FIG. 2**

**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/US2012/07Q811

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. C08G77/08 C08G77/58 C08L83/04 C09D183/04 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) C08L C09D C08G		
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) EPO-Internal , WPI Data		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
<b>Category*</b>	<b>Citation of document, with indication, where appropriate, of the relevant passages</b>	<b>Relevant to claim No.</b>
X	US 5 677 411 A (WARD BRIAN J [US] ET AL) 14 October 1997 (1997-10-14) col umn 3, line 63 - col umn 6, line 31 col umn 10, line 57 - col umn 11, line 30 col umn 9, line 39 - col umn 10, line 9 claim 11 -----	1-12
X	US 2002/156186 AI (BUBLEWITZ ALEXANDER [DE] ET AL) 24 October 2002 (2002-10-24) paragraphs [0154] - [0155] paragraphs [0098] - [0099] exampl es 3-6 -----	1-11
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> 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 13 February 2013		Date of mailing of the international search report 27/02/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer St i nch combe, John

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/07Q811

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5677411	A	14-10-1997	DE 19625563 AI 02-01-1997
			FR 2736060 AI 03-01-1997
			GB 2302876 A 05-02-1997
			JP 9143368 A 03-06-1997
			US 5677411 A 14-10-1997
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US 2002156186	AI	24-10-2002	US 2002156186 AI 24-10-2002
			US 2005239958 AI 27-10-2005
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