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(54) Title: LOW TVOC RELEASE SILICONE COMPOSITE SHEET

(57) Abstract: The disclosure relates to a low TVOC release silicone composite sheet, comprising: 1) a substrate layer selected from a fabric or a polymeric film. 2) a silicone adhesive layer coated onto the substrate layer and containing volatile organic compound (VOC) releasing additives, and 3) a reinforcing layer adjacent to the silicone adhesive layer; wherein the coating amount of the silicone adhesive layer is less than 45 wt%, preferably less than 35 wt%, more preferably less than 20 wt%, based on the total coating amount of the silicone adhesive layer and the reinforcing layer. and wherein both silicone adhesive layer and reinforcing layer contain or consist essentially of liquid silicone rubber (LSR) or room temperature vulcanized silicone rubber (RTV), and said reinforcing layer contains one or more coatings comprising A). organopolysiloxane having one or more silicon atom-bonded alkenyl groups on average in one molecule; B). an organohydrogenpolysiloxane; and C). a hydrosilylation reaction catalyst present in any amount effective to cure the composition. Furthermore, it relates also to a method for coating and for reducing TVOC release.



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LOW TVOC RELEASE SILICONE COMPOSITE SHEET

Technical field

- 5 The disclosure relates to a low TVOC release silicone composite sheet, a method for coating and use of the method for reducing TVOC release.

Prior art

- 10 Because of the environmental damage that can be caused from VOC (volatile organic compounds), there are various regulations that limit the use of coatings with high VOC release.

Higher standard on TVOC (total volatile organic compounds) release for total car modulus is required. Especially, the coated fabric for air bag with high coat weight like 100 gsm to 200 gsm
15 is highlighted to pass the level of less than 50ugC/g. The high weight coated fabric is mainly used for heat resistant sheet. Most of the existing coating products cannot reach this industry standard.

CN 104768743 A discloses an inflatable vehicle safety device including e.g. air bag in which a
20 barrier layer may be adjacent to the fabric layer and includes at least one layer of silicone elastomer and one or more topcoats. This reference focuses on the heat resistance but fails to pay attention to reduce VOC release.

Besides, for abrasion resistant artificial leather coated with silicone composition, TVOC also
25 becomes a difficult topic. Currently, the skilled persons have not found efficient method to reduce the TVOC level to about 100ugC/g or less.

One feasible method in the prior art to reduce the VOC release amount may probably be baking
30 which requires however longer curing time and/or higher curing temperature. Even if subjected to such a baking or curing treatment, the composite sheet may probably be still not compliant with the strict regulations on VOC release. In case of high coat weight coating, the situation is worse since more VOC-releasing additives are contained in the adhesive layers.

An efficient method to reduce TVOC release is urgently required to satisfy the new standard and
35 strict regulations, especially in case of high coat weight coating.

Presentation of the disclosure

It is an object of the present disclosure, therefore, to provide a composite sheet which releases
40 lower TVOC but still maintaining good adhesion to the substrate and thus good mechanical property. This object, surprisingly, is achieved with the composite sheet as described in claim 1.

Another object is to provide a method of coating during which lower TVOC is released and the

adhesion is not impaired. With this method, harsher curing or baking conditions are not required any more to reduce TVOC release. This object can be also achieved by the method as described in claim 15.

5 Definitions

As used herein, the term “low TVOC composition” means that the composition contains no more than 100ugC/g of total volatile organic compounds per gram of the cured coating composition.

10 As used herein, the term “volatile organic compound” refers to compounds that have at least one carbon atom and which are released from the cured composition. Examples of “volatile organic compounds” include, but are not limited to, alcohols, benzenes, toluenes, chloroforms, and cyclohexanes. In particular in the fabric for preparing airbags or artificial leather products which are to be coated with silicone composition, the VOC mainly comes from alcohol from silane,
15 volatiles in the silicone oils, silicone resin etc.

As used herein, the term “high coat weight coating” means that the weight of the coating composition on the unit area after curing or after drying per unit area not less than 90 gram square meter, preferably 100gsm-400gsm.

20 As used herein, when referring to a composition or component, such as the organopolysiloxane or a polysiloxane resin, the term “consisting (or consists) essentially of” means that the concerned component or composition comprises more than 50% by weight, for example, at least 60% by weight, at least 70% by weight, or at least 80%, 90% or 95% by weight, or even 100%
25 by weight of the indicated ingredient or component respectively, based on the total weight of the concerned component or composition respectively.

In a first aspect of the present disclosure, a composite sheet is provided, comprising:

- 1) a substrate layer selected from a fabric or a polymeric film.
 - 30 2) a silicone adhesive layer coated onto the substrate layer and containing volatile organic compound (VOC) releasing additives, and
 - 3) a reinforcing layer adjacent to the silicone adhesive layer;
- wherein the coating amount of the silicone adhesive layer is less than 45 wt%, preferably less than 35 wt%, more preferably less than 20 wt%, based on the total coating amount of
35 the silicone adhesive layer and the reinforcing layer.
- and wherein both silicone adhesive layer and reinforcing layer contain or consist essentially of liquid silicone rubber (LSR) or room temperature vulcanized silicone rubber (RTV), and
- said reinforcing layer contains one or more coatings comprising
- 40 A). organopolysiloxane having one or more silicon atom-bonded alkenyl groups on average in one molecule;
 - B). an organohydrogenpolysiloxane; and
 - C). a hydrosilylation reaction catalyst present in any amount effective to cure the

composition.

5 In the prior art, the material compositions of the silicone adhesive layer and the reinforcing layer as defined in the context of this disclosure are usually simply and homogeneously mixed by the skilled person to form an adhesive layer coated on the substrate like airbags or artificial leathers. Then they are baked or cured at a relatively high temperature within a long time to release as much VOC as possible. However, the inventor has unexpectedly found that the amount of released TVOC can be notably reduced without harsh curing and baking conditions while still maintaining good mechanical property like cohesive strength, provided that the usual adhesive
10 coating is designed as a two-layer structure as defined above and the VOC-releasing additives are contained in the silicone adhesive layer and its coating amount is less than 45 wt% as required above. The TVOC release will be reduced to less than 100 μ gC/g, preferably less than 70 μ gC/g, more preferably less than 50 μ gC/g.

15 In the present disclosure, the substrate layer can be a fabric including a woven fabric or a nonwoven fabric, or a polymeric film selected from polypropylene, polyethylene, fiberglass, polyamides, poly(ethylene) terephthalate, and compositions or mixtures thereof. The woven fabric may have threads with a thickness that is advantageously equal to or greater than 20 dtex. When the fabric is a nonwoven fabric, it may have a basis weight between about 40 g/m² and
20 about 400 g/m². When the nonwoven fabric is used as the substrate layer, it is preferably an artificial leather.

In one embodiment of the disclosure, it has been found that the inventive method and composite sheet are most suitable for the substrate which is air bag or artificial leather or at least part of
25 them. During the preparation of air bags or artificial leathers according to the present disclosure, much less TVOC would be released compared with the prior art under the same treatment conditions such as baking temperature and curing duration.

The silicone adhesive layer is a first layer directly applied on the substrate. In one beneficial
30 embodiment, it contains or consists essentially of liquid silicone rubber (LSR) or room temperature vulcanized silicone rubber (RTV), including without limitation any base material.

In one embodiment, the silicone adhesive layer is a composition including:

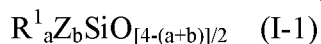
- 35 A). organopolysiloxane having one or more silicon atom-bonded alkenyl groups on average in one molecule;
- B). an organohydrogenpolysiloxane;
- C). a hydrosilylation reaction catalyst present in any amount effective to cure the composition;
- 40 D). VOC-releasing additives.

Component A) Organopolysiloxane

In the present disclosure, the alkenyl group in the organopolysiloxane may be at any position on the main chain of the polysiloxane, for example at the end or in the middle or at both ends and in
45 the middle of the molecular chain.

In one beneficial embodiment of the disclosure, the organopolysiloxane comprises:

(i) siloxane units of formula (I-1)



wherein

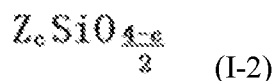
5 R^1 represents C_2 - C_{12} , preferably C_2 - C_6 alkenyl, most preferably vinyl or allyl,
 Z may be the same or different and represent a monovalent hydrocarbon radical having from 1 to 30, preferably from 1 to 12 carbon atoms, including alkyl groups optionally substituted by at least one halogen atom, preferably selected from C_1 to C_8 alkyl groups, and also including aryl groups, especially C_6 to C_{20} aryl groups,

10 a is 1 or 2,

b is 0, 1 or 2 and

the sum of $a + b$ is 1, 2 or 3, and

(ii) optionally other siloxane units of formula (I-2)



15 wherein

Z has the meaning as described above and c is 0, 1, 2 or 3.

20 In a preferred embodiment, Z may be selected from the group consisting of methyl, ethyl, propyl, 3,3,3-trifluoropropyl, phenyl, xylyl and tolyl and the like. Preferably, at least 60 mol% of the group Z is methyl.

25 The organopolysiloxane may have a viscosity of at least equal to 50 mPa.s and preferably less than 200,000 mPa.s. In the present disclosure, all viscosity data are concerned with dynamic viscosity values and can be measured, for example, in a known manner at 20°C using a Brookfield instrument, unless otherwise specified.

The organopolysiloxane may be formed only from the units of formula (I-1) or may additionally comprise units of formula (I-2). The organopolysiloxane may be a linear, branched or cyclic structure.

30 Examples of the siloxane units of formula (I-1) include vinyl dimethylsiloxy, vinylphenylmethylsiloxy, vinyl methylsiloxy and vinyl siloxane units.

35 Examples of the siloxane units of formula (I-2) include $SiO_{4/2}$ units, dimethylsiloxy, methylphenylsiloxy, diphenylsiloxy, methylsiloxy and phenylsiloxy units.

40 Examples of the organopolysiloxane include straight or cyclic compounds such as dimethylpolysiloxane (including dimethylvinylsilyl end group), (methylvinyl) (dimethyl) polysiloxane copolymers (including trimethylsilyl end group), (methylvinyl) (dimethyl) polysiloxane copolymers (including dimethylvinylsilyl end group) and cyclic methyl vinyl polysiloxane.

In one more preferable embodiment, especially low TVOC release with very stable adhesion to the substrate is found if the organopolysiloxane comprises at least two different siloxane units

selected from the group consisting of siloxane units M of formula $R_3SiO_{1/2}$, siloxane units D of formula $R_2SiO_{2/2}$, siloxane units T of formula $RSiO_{3/2}$ and siloxane units Q of formula $SiO_{4/2}$, wherein R represents a monovalent hydrocarbon group having from 1 to 20 carbon atoms, and with the proviso that at least one of these siloxane units is the siloxane unit T or Q and at least one of the siloxane units M, D and T comprises an alkenyl group.

As for the organopolysiloxane comprising the siloxane units M (M^{Vi} units) having alkenyl groups, it is possible to use a polysiloxane resin selected from the group consisting of the following organopolysiloxane resins (in the context, when mentioning the unit T, Q or D, the unit with the superscript "Vi" represents the unit containing alkenyl group):

- an organopolysiloxane resin of formula $M^{Vi}Q$ consisting essentially of the following units: monovalent siloxane units M^{Vi} of formula $R'R_2SiO_{1/2}$, and tetravalent siloxane units Q of formula $SiO_{4/2}$, and
 - an organopolysiloxane resin of formula $MM^{Vi}Q$ consisting essentially of the following units: monovalent siloxane units M of formula $R_3SiO_{1/2}$, and monovalent siloxane units M^{Vi} of formula $R'R_2SiO_{1/2}$, and tetravalent siloxane units Q of formula $SiO_{4/2}$, and
 - an organopolysiloxane resin of formula $M^{Vi}T^{Vi}Q$ consisting essentially of the following units:
 - (a) monovalent siloxane units M^{Vi} of formula $R'R_2SiO_{1/2}$,
 - (b) trivalent siloxane units T^{Vi} of formula $R'SiO_{3/2}$, and
 - (c) tetravalent siloxane units Q of formula $SiO_{4/2}$,
 - an organopolysiloxane resin of formula $M^{Vi}TQ$ consisting essentially of the following units: trivalent siloxane units T of formula $RSiO_{3/2}$; monovalent siloxane units M^{Vi} of formula $R'R_2SiO_{1/2}$, and tetravalent siloxane unit Q of formula $SiO_{4/2}$, and
 - an organopolysiloxane resin of formula $M^{Vi}DQ$ consisting essentially of the following units: divalent siloxane units D of formula $R_2SiO_{2/2}$; monovalent siloxane units M^{Vi} of formula $R'R_2SiO_{1/2}$, and tetravalent siloxane units Q of formula $SiO_{4/2}$,
- wherein R represents a monovalent hydrocarbon group having from 1 to 20 carbon atoms, preferably a monovalent aliphatic or aromatic hydrocarbon group having preferably from 1 to 12, more preferably from 1 to 8 carbon atoms, and R' represents an alkenyl group, preferably an alkenyl group having from 2 to 12, more preferably from 2 to 6 carbon atoms, particularly vinyl or allyl, and most preferably vinyl.

As for the organopolysiloxane comprising the siloxane units D (D^{Vi} units) having alkenyl groups, it is possible to use a polysiloxane resin selected from the group consisting of:

- an organopolysiloxane resin of formula $MD^{Vi}Q$ consisting essentially of the following units: divalent siloxane units M of formula $R_2SiO_{2/2}$; monovalent siloxane units D^{Vi} of formula $R'R_2SiO_{1/2}$, and tetravalent siloxane units Q of formula $SiO_{4/2}$,
- wherein R represents a monovalent hydrocarbon group having from 1 to 20 carbon atoms, preferably a monovalent aliphatic or aromatic hydrocarbon group having preferably from 1 to 12, more preferably from 1 to 8 carbon atoms, and

R' represents an alkenyl group, preferably an alkenyl group having from 2 to 12, more preferably from 2 to 6 carbon atoms, particularly vinyl or allyl, and most preferably vinyl.

5 Furthermore, the organopolysiloxane resin comprising the siloxane units D (D^{Vi} units) having alkenyl groups may be also selected from organopolysiloxane resins of formula $MD^{Vi}TQ$.

In one most preferable embodiment, the organopolysiloxane may be selected from organopolysiloxane resins of formula $MM^{Vi}Q$ and/or formula $MD^{Vi}Q$.

10 Component B) Organohydrogensiloxane

The organohydrogensiloxane in the silicone composition functions as a curing agent, such that the silicon-bonded hydrogen atoms in the organohydrogensiloxane react with the alkenyl radicals of the organopolysiloxane. The silicon-bonded hydrogen atoms in the organohydrogensiloxane may also be used to generate hydrogen gas for foaming the composition when desirable. Organohydrogensiloxanes that may be used contain an average of at least one silicon-bonded hydrogen atoms in chain per molecule.

20 The organohydrogensiloxane can have a linear, cyclic, or branched structure, and can be a homopolymer, a copolymer, mixtures of two or more different homopolymers, mixtures of two or more different copolymers or mixtures of these types of polymers.

The amount of the organohydrogensiloxane used should be sufficient to provide the desired degree of crosslinking during cure. Generally, the proportion of the organohydrogensiloxane will be within the range of from about 2 to about 80 parts, and alternatively from about 3 to about 40 parts by weight per 100 parts by weight of the organopolysiloxane.

Component C) Hydrosilylation reaction catalyst

30 The hydrosilylation reaction catalyst may comprise a platinum group metal catalyst including any rhodium, ruthenium, palladium, osmium, iridium or platinum-containing catalysts known to one skilled in the art to facilitate hydrosilylation reactions. It is preferred to use compounds of platinum and rhodium. The complexes and organic products of platinum described, for example, in the patents US-A-3 159 601, US-A-3 159 602, US-A-3 220 972, EP-A-0 057 459, EP-A-0 188 978 and EP-A-0 190 530, and in particular, the complexes of platinum with vinyl organosiloxane described, for example, in the patents US-A-3 419 593, US-A-3 715 334, US-A-3 377 432 and US-A-3 814 730, can be used. These patents are hereby incorporated by reference in their entirety.

40 In one embodiment, the platinum-containing catalyst is a platinum catalyst. Suitable forms of a platinum catalyst include but are not limited to chloroplatinic acid, 1,3-diethenyl-1,1,2,2-tetramethyldisiloxane platinum complex, complexes of platinum halides or chloroplatinic acid with divinylsiloxane and complexes formed by the reaction of chloroplatinic acid, divinyltetramethyldisiloxane and tetramethyldisiloxane.

45 The amount of the hydrosilylation catalyst used such as the platinum catalyst is generally

ranging from 0.1 to 10000 ppm, preferably 1 to 1000 ppm and more preferably 5 to 500 ppm based on the weight of the organopolysiloxane.

Component D) VOC-releasing additives

5
According to our disclosure, it is preferable that most of or all of the VOC-releasing additives are merged in the adhesive layer and the rest or none of them are contained in the second layer, i.e. reinforcing layer. Herein, the expression “most of or all of the VOC-releasing additives” refers to at least 60%, or preferably at least 70% or 80% or 90% or 95% or more preferably 100% of the
10 total amount of VOC-releasing additives (that are required in the silicone adhesive and reinforcing layers but finally releases less than 100 µgC/g of TVOC according to the present disclosure). The VOC-releasing additives may include flavor agent, color paste, adhesive promotor or mixture thereof. Furthermore, the VOC-releasing additives may also include some fillers treated with VOC-releasing substance. Among the VOC-releasing additives, the adhesive
15 promotor is an important one which releases a notable amount of VOC.

In one embodiment of the disclosure, the VOC-releasing additives are adhesive promoters which may be consisting essentially of one or more members selected from the group comprising:

- 20 – a vinyl-based silane or organosiloxane alone or partially hydrolyzed and also one of its reaction products;
- a silane or organosiloxane functionalized by an epoxy functional group alone or partially hydrolyzed and also one of its reaction products;
- a methacrylate-functional silane or organosiloxane alone or partially hydrolyzed and also one of its reaction products;
- 25 – a silane or organosiloxane functionalized by an anhydride radical alone or partially hydrolyzed and also one of its reaction products; and
- a butyl titanate type chelate.

In another embodiment of the disclosure, the adhesive promoter may be one or more selected
30 from epoxy silane, alkoxy silane, acyloxy silane, aryloxy silane or oligomers thereof. They include, but are not limited to, 3-glycidoxypropyl trimethoxy silane, octyltriethoxysilane, vinyltriethoxysilane, vinyltrimethoxysilane, gamma-methacryloxy-propyltrimethoxysilane, beta-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane
beta-(3,4-epoxycyclohexyl)-ethyltriethoxysilane and bis (trimethoxysilyl propyl) fumarate,
35 alkoxy or aryloxy silicones such as trimethoxysilyl functional groups modified silicones. Furthermore, they also include silanols, oligosiloxanes containing one or more alkoxy silyl functional group, polysiloxanes containing alkoxy silyl functional group, one or more oligomeric siloxanes containing hydroxyl functional groups, polysiloxanes containing one or more aryloxy silyl functional group, cyclosiloxanes containing one or more alkoxy silyl functional group,
40 cyclosiloxanes containing one or more hydroxyl groups, tetra-alkoxy silanes, vinyltrimethoxysilane, and mixtures thereof, and combinations thereof.

In one beneficial embodiment, the invention is found very effective to reduce TVOC if the VOC-releasing additives are or contain adhesive promoters which are

- 45 preferably selected from a vinyl-based silane or organosiloxane alone or partially hydrolyzed and also one of its reaction products, and a silane or organosiloxane

functionalized by an epoxy functional group alone or partially hydrolyzed and also one of its reaction products; and

more preferably selected from epoxy silan, alkoxy silane, aryloxy silane or oligomers thereof; and

5 most preferably selected from 3-glycidoxypropyl trimethoxy silane, octyltriethoxysilane, vinyltriethoxysilane, vinyltrimethoxysilane, gamma-methacryloxy-propyltrimethoxysilane, beta-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane and beta-(3,4-epoxycyclohexyl)-ethyltriethoxysilane.

10

In one embodiment, the amount of the VOC-releasing additives, preferably adhesive promoters are from 0.01 to 5 parts, preferably 1 to 3 parts by weight per 100 parts by weight of component A organopolysiloxane.

15 The silicone adhesive layer is set as an adherent medium between the reinforcing layer and the substrate, and its coat weight must be controlled at a relative low level so that the contribution to the total carbon release is very limited. In one embodiment, the coat weight of the silicone adhesive layer is of 5 gsm-200 gsm, such as 10-150gsm.

20 According to the present disclosure, a reinforcing layer is arranged adjacent to the adhesive layer. The reinforcing layer may be consisting of one or more coatings which are preferably coatings of a silicon-based composition. Such a silicon-based composition may preferably also comprise component A') organopolysiloxane, component B') organohydrogensiloxane, and optional component C') a hydrosilylation reaction catalyst. Herein, the general descriptions and
25 preferable embodiments given for the components A) to C) of the adhesive layer apply respectively to the components A') to C') of the reinforcing layer.

In the instant application, the reinforcing layer may contain a top coat, which is the outmost coating of the composite sheet and may be different from the other coatings in the reinforcing
30 layer with regard to the composition. Thus the reinforcing layer can play the role as heat resistance, abrasion resistance or surface low coefficient friction. Preferably, the reinforcing layer here including the outmost top coat (if present) is a silicone composition and thus is capable of forming a silicone coat upon curing.

35 In one preferable embodiment, the reinforcing layer may have the same or different composition as the adhesive layer does except that less VOC-releasing additives are contained in the reinforcing layer.

In one preferable embodiment, the coat weight of the reinforcing layer is of 80 – 300 gsm, e.g.
40 100 – 200 gsm.

There also could be an optional surface treatment on the reinforcing layer for less coefficient of friction and better heat resistance.

The total coating weight of substrate is more than 50gsm, preferably 100gsm-300gsm.

5 When the substrate is airbag, the total weight of the adhesive layer and reinforcing layer is of 90-300gsm, among which the adhesive layer is of 10gsm-80gsm, optional 20-50gsm; and the second layer is of 80gsm-200gsm, optional 100gsm-180gsm.

10 When the substrate is artificial leather, the total weight of the adhesive layer and reinforcing layer is of 200-400gsm, among which first layer is of 50gsm-200gsm, optional 80-120gsm; and the second layer is of 100gsm-300gsm.

15 In one preferable embodiment of the disclosure, the adhesive layer is directly arranged between the substrate and the reinforcing layer. In another preferable embodiment, the composite sheet is composed of the substrate, the silicone adhesive layer and the reinforcing layer as defined above, wherein the adhesive promoters, preferably those releasing VOC, are contained only in the silicone adhesive layer.

20 Depending on the various applications, the composition of either silicone adhesive layer or reinforcing layer may further comprise component E), other additives that do not release VOC. These additives are known to the skilled person.

25 In one embodiment, the composition of the silicone composition of adhesive layer or reinforcing layer may contain a non-VOC-releasing filler material such as a reinforcing filler or a non-reinforcing filler, preferably a non-reinforcing mineral filler. Such filler materials may include, but not be limited to, various amorphous or crystalline inorganic compounds, such as fumed silica, precipitated silica, quartz, wollastonite, glass bead, talc, Kaolin, Mica or calcium carbonate etc.; and metal oxides such as alumina, hydrated alumina, ferric oxide and titanium dioxide; or mixtures thereof.

30 The amount of these non-VOC-releasing additives, in particular filler material such as the fibrous materials added to the silicone composition may e.g. range from 5 to 40 parts, prefer 10 to 35 parts by weight per 100 parts by weight of the organopolysiloxane.

In another aspect of the disclosure, it relates to a method for coating, comprising the following steps:

35 - providing a substrate,
 - applying a silicone adhesive layer on the substrate, and
 - applying a reinforcing layer on the adhesive layer;
 wherein said substrate, adhesive layer and reinforcing layer are as defined above and the coating amount of the silicone adhesive layer is less than 45 wt%, preferably less than 35 wt%,
40 more preferably less than 20 wt%, based on the total coating amount of the silicone adhesive layer and the reinforcing layer.

45 In one preferable embodiment of the inventive method, the adhesive layer is coated directly onto the substrate, preferably airbags and artificial leathers, and then after curing of the adhesive layer the reinforcing layer is coated directly onto the adhesive layer.

ExamplesTVOC Test Equipment: HS-GC/FID5 TVOC Test condition:

Prior to weighing, these materials shall be cut into pieces and dried for 24h over calcium chloride.

- 10 The specimen shall be removed at the indicated location from the material across the full cross section of the specimen. Then they shall be cut to pieces with a weight between 10mg and 25mg without increasing the temperature of the specimen.

- 15 The specimen parts are weighed in a head space vial (min. 3vials per specimen). The vial is sealed gas-tight using a Teflon-coated septum facing the inside of the vial.

TVOC Testing method:

- 20 Prior to measurement the vials are conditioned in the air above the sample for 5 hours \pm 5minutes at $120^{\circ}\text{C} \pm 1^{\circ}\text{C}$ in the head space sampling valve in order to enrich the vial with the substances contained in the sample, immediately afterwards the vials shall be analyzed. At least 3 samples shall be analyzed.

- 25 The blank value is determined by calculating the mean value taking signal values from at least 3 measurements with empty vials.

Dosage shall be identical and reproducible for all sample analyses, blank value and calibrating solution.

- 30 The separating column shall be heated up to maximum temperature for at least 15minutes once a week.

Adhesion test method:

Adhesion test is carried out according to the following steps:

- 35 Step 1: Coating first layer on 470dtex nylon 66 fabric 46*46/cm with knife coater, coating weight 25gsm-30gsm, curing at $160^{\circ}\text{C} * 2\text{min}$;
 Step 2: Coating 1mm thickness*5mm length*1cm width second layer between two pieces of first layer coated fabric, curing at $160^{\circ}\text{C} * 2\text{min}$;
 Step 3: Peel the cookies, record the maximum force and failure mode;
 40 Standard: 100% cohesion failure mold requested;
 Step 4: aging the cookies at $70^{\circ}\text{C} * 95\% \text{RH}$ at 17days;
 Step 5: test the peeling, record the maximum force and failure mode.

Testing sample preparation:

- 45 Mix first part and second part evenly, knife coating or layer bar coating the first layer on the

fabric with requested coat weight and cure for 160°C*2min (for airbag) or 110°C*6min (for artificial leather), then coat the second layer on top of the first layer, with requested coat weight and curing condition.

5 Example 1, 2 and Comparative Examples

Component A1:

mixture of MM^{Vi}Q resin (vinyl content 0.041%) and vinyl terminal-polydimethylsiloxane oil, vinyl content 0.003%, viscosity 60,000mpas;

10 Component A2:

mixture of MD^{Vi}Q resin (vinyl content 0.028%) and vinyl terminal-polydimethylsiloxane oil, vinyl content 0.003%, viscosity 100,000mpas;

Component B:

methyl terminal-polymethylhydrogensiloxane with SiH content of 0.69mol/100g;

15 Component C:

Bluestar Silicones Silcolease Catalyst 21093, Bluestar Silicones

Component D:

Mixture of 3-glycidoxypropyl trimethoxy silane and butyl titanate;

component E:

20 calcium carbonated

Example 1

Preparation for the second layer (reinforcing layer):

100 parts component A2, 7 parts component B by weight of per 100 parts component A2, 0.027
25 parts component C by weight of per 100 parts component A2, 18.9 parts component E by weight
of per 100 parts component A2

Coat weight: 155gsm

Curing condition: 160°C*2min

30 Preparation for the first layer (silicone adhesive layer):

100 parts component A2, 7 parts component B by weight of per 100 parts component A2, 2.8
parts component D by weight of per 100 parts component A2, 0.027 parts component C by
weight of per 100 parts component A2, 18.9 parts component E by weight of per 100 parts
component A2.

35 Substrate: 470dtex nylon 66 fabric

Coat weight: 25gsm

Curing condition: 160°C*2min

Example 2

40 Preparation for the second layer (reinforcing layer):

100 parts component A1, 7 parts component B by weight of per 100 parts component A1, 0.022
parts component C by weight of per 100 parts component A1; 26 parts component E by weight
of per 100 parts component A1.

Coat weight: 155gsm

45 Curing condition: 160°C*2min

Preparation for the first layer (silicone adhesive layer):

100 parts component A2, 7 parts component B by weight of per 100 parts component A2, 2.8 parts adhesive promoter D by weight of per 100 parts component A2, 0.027 parts component C by weight of per 100 parts component A2, 18.9 parts component E by weight of per 100 parts component A2.

Substrate: 470dtex nylon 66 fabric

Coat weight: 25gsm

Curing condition: 160°C*2min

10 Comparative Example 1:

Preparation: 100 parts component A1, 7 parts component B by weight of per 100 parts component A1, 4.64 parts adhesive promoter D by weight of per 100 parts component A1, 0.022 parts component C by weight of per 100 parts component A1, 26 parts component E by weight of per 100 parts component A1, mixed as second part.

15 Substrate: 470dtex nylon 66 fabric

Coat weight: 155gsm

Curing condition: 160°C*4min

Comparative Example 2:

20 Preparation: 100 parts component A2, 7 parts component B by weight of per 100 parts component A2, 2.8 parts adhesive promoter D by weight of per 100 parts component A2, 0.027 parts component C by weight of per 100 parts component A2, 18.9 parts component E by weight of per 100 parts component A2, mixed as second part.

Substrate: 470dtex nylon 66 fabric

25 Coat weight: 180gsm

Curing condition: 160°C*4min

Comparative Example 3:

30 Preparation: 100 parts component A2, 7 parts component B by weight of per 100 parts component A2, 2.8 parts adhesive promoter D by weight of per 100 parts component A2, 0.027 parts component C by weight of per 100 parts component A2, 18.9 parts component E by weight of per 100 parts component A2, mixed as second part.

Substrate: 470dtex nylon 66 fabric

Coat weight: 200gsm

35 Curing condition: 160°C*4min + 200°C*4min

Table 1 Composition and curing condition for Example 1, 2 and comparative example 1, 2 and 3

First layer	Ex 1	Ex 2	Comparative Ex 1	Comparative Ex 2	Comparative Ex 3
A1	/	/	100	/	/
A2	100	100	/	100	100
B	7	7	7	7	7
C	0.027	0.027	0.022	0.027	0.027
E	18.9	18.9	26	18.9	18.9
D	2.8	2.8	4.64	2.8	2.8
Coat weight	25gsm	25gsm	155gsm	180gsm	200gsm

Curing condition	160°C*2min	160°C*2min	160°C*4min	160°C*4min	160°C*4min + 200°C*4min
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Second layer	Ex 1	Ex 2	Comparative Ex 1	Comparative Ex 2	Comparative Ex 3
A1	/	100	NA	NA	NA
A2	100	/			
B	7	7			
C	0.027	0.022			
E	18.9	26			
D	/	/			
Coat weight	155gsm	155gsm			
Curing condition	160°C*2min	160°C*2min			

Table 2 TVOC Test results for all examples:

	Example 1	Example 2	Comparative Ex 1	Comparative Ex 2	Comparative Ex 3
First Layer (gsm)	25gsm	25gsm	/	/	/
Second layer (gsm)	155gsm	155gsm	/	/	/
Total (gsm)	180gsm	180gsm	155gsm	180gsm	200gsm
TVOC (ugC/g)	65.6ugC/g	30.0ugC/g	230.9ugC/g	158.3ugC/g	55.9ugC/g

5 Table 3 Adhesive test results for Example 2

Initial

First layer coat weight (gsm)	Second layer thickness(mm)	Cohesive (%)
24gsm	0.65	100%
37gsm	0.7	100%

After 70°C 95% 2 weeks aging

Adhesive layer coat weight (gsm)	Second layer thickness(mm)	Cohesive (%)
26gsm	0.8	100%
37gsm	0.9	100%

10 In all, as can be seen from the above results, the inventive composite sheet (two layers) have much lower TVOC release than the traditional signal layer structure (one layer). In the meantime, the cohesive strength is still maintained in a high level and has good stable adhesion.

According to the result, if the amount of first layer is more than 45% (based on the total coating

amount of the silicone adhesive layer and the reinforcing layer), although the TVOC also could be reduced with longer curing time and/or higher curing temperature, this is difficult to realize and not practical in industry.

Claims

1. A composite sheet, comprising:
 - 1) a substrate layer selected from a fabric or a polymeric film.
 - 2) a silicone adhesive layer coated onto the substrate layer and containing volatile organic compound (VOC) releasing additives, and
 - 3) a reinforcing layer adjacent to the silicone adhesive layer;wherein the coating amount of the silicone adhesive layer is less than 45 wt%, preferably less than 35 wt%, more preferably less than 20 wt%, based on the total coating amount of the silicone adhesive layer and the reinforcing layer.
and wherein both silicone adhesive layer and reinforcing layer contain or consist essentially of liquid silicone rubber (LSR) or room temperature vulcanized silicone rubber (RTV), and
said reinforcing layer contains one or more coatings comprising
 - A). organopolysiloxane having one or more silicon atom-bonded alkenyl groups on average in one molecule;
 - B). an organohydrogenpolysiloxane; and
 - C). a hydrosilylation reaction catalyst present in any amount effective to cure the composition.
2. The composite sheet as claimed in claim 1, characterized in that the substrate is a fabric selected from a woven fabric, a nonwoven fabric, or a polymeric film selected from polypropylene, polyethylene, fiberglass, polyamides, poly(ethylene) terephthalate, and compositions or mixtures thereof; preferably selected from air bag or artificial leather or at least part of them.
3. The composite sheet as claimed in either of preceding claims, characterized in that its total volatile organic content (TVOC) release is less than 100 $\mu\text{gC/g}$, preferably less than 70 $\mu\text{gC/g}$, more preferably less than 50 $\mu\text{gC/g}$.
4. The composite sheet as claimed in either of preceding claims, characterized in that at least 60%, or preferably at least 70% or 80% or 95% or more preferably 100% of the total amount of VOC-releasing additives are contained in the silicone adhesive layer.
5. The composite sheet as claimed in either of preceding claims, characterized in that the VOC-releasing additives are adhesive promoters which are selected from a vinyl-based silane or organosiloxane alone or partially hydrolyzed and also one of its reaction products, and a silane or organosiloxane functionalized by an epoxy functional group alone or partially hydrolyzed and also one of its reaction products; preferably selected

from epoxy silane, alkoxy silane, aryloxy silane or oligomers thereof; and more preferably selected from 3-glycidoxypropyl trimethoxy silane, octyltriethoxysilane, vinyltriethoxysilane, vinyltrimethoxysilane, gamma-methacryloxy-propyltrimethoxysilane, beta-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane, and beta-(3,4-epoxycyclohexyl)-ethyltriethoxysilane.

6. The composite sheet as claimed in either of preceding claims, characterized in that the silicone adhesive layer contains or consists essentially of liquid silicone rubber (LSR) or room temperature vulcanized silicone rubber (RTV), preferably is a composition including:
 - A). organopolysiloxane having one or more silicon atom-bonded alkenyl groups on average in one molecule;
 - B). an organohydrogenpolysiloxane;
 - C). a hydrosilylation reaction catalyst present in any amount effective to cure the composition; and
 - D). VOC-releasing additives, preferably adhesive promoters.

7. The composite sheet as claimed in claim 6, characterized in that the amount of the VOC-releasing additives, preferably adhesive promoters are from 0.01 to 5 parts, preferably 1 to 3 parts by weight per 100 parts by weight of component A organopolysiloxane.

8. The composite sheet as claimed in claim 6, characterized in that the organopolysiloxane comprises at least two different siloxane units selected from the group consisting of siloxane units M of formula $R_3SiO_{1/2}$, siloxane units D of formula $R_2SiO_{2/2}$, siloxane units T of formula $RSiO_{3/2}$ and siloxane units Q of formula $SiO_{4/2}$, wherein R represents a monovalent hydrocarbon group having from 1 to 20 carbon atoms, and with the proviso that at least one of these siloxane units is the siloxane unit T or Q and at least one of the siloxane units M, D and T comprises an alkenyl group.

9. The composite sheet as claimed in claim 6, characterized in that said organopolysiloxane is an organopolysiloxane resin of formula $MM^{Vi}Q$ consisting essentially of the following units:
 - monovalent siloxane units M of formula $R_3SiO_{1/2}$;
 - monovalent siloxane units M^{Vi} of formula $R'R_2SiO_{1/2}$, and
 - tetravalent siloxane units Q of formula $SiO_{4/2}$;
 wherein R represents a monovalent hydrocarbon group having from 1 to 20 carbon atoms, preferably a monovalent aliphatic or aromatic hydrocarbon group having preferably from 1 to 12, more preferably from 1 to 8 carbon atoms, and R' represents an alkenyl group, preferably an alkenyl group having from 2 to 12, more

- preferably from 2 to 6 carbon atoms, particularly vinyl or allyl, and most preferably vinyl.
10. The composite sheet as claimed in claim 6, characterized in that said organopolysiloxane is an organopolysiloxane resin of formula $MD^{Vi}Q$ consisting essentially of the following units:
divalent siloxane units M of formula $R_2SiO_{2/2}$;
monovalent siloxane units D^{Vi} of formula $R'R_2SiO_{1/2}$, and
tetravalent siloxane units Q of formula $SiO_{4/2}$;
wherein R represents a monovalent hydrocarbon group having from 1 to 20 carbon atoms, preferably a monovalent aliphatic or aromatic hydrocarbon group having preferably from 1 to 12, more preferably from 1 to 8 carbon atoms, and
R' represents an alkenyl group, preferably an alkenyl group having from 2 to 12, more preferably from 2 to 6 carbon atoms, particularly vinyl or allyl, and most preferably vinyl.
 11. The composite sheet as claimed in either of preceding claims, characterized in that the total coating weight of the adhesive layer and the reinforcing layer is more than 50 gsm, preferably 100 to 400 gsm, more preferably 100 to 300 gsm.
 12. The composite sheet as claimed in either of preceding claims, characterized in that in case of the substrate being airbag the total weight of the adhesive layer and the reinforcing layer is 90 to 300 gsm, and/or
that in case of the substrate being artificial leather, the total weight of the adhesive layer and the reinforcing layer is 200 to 400 gsm.
 13. The composite sheet as claimed in either of preceding claims, characterized in that is composed of said substrate, said silicone adhesive layer and said reinforcing layer, wherein the adhesive promoters, preferably VOC-releasing promoters, are contained only in the silicone adhesive layer.
 14. A method for coating, comprising the following steps:
 - providing a substrate,
 - applying an adhesive layer on the substrate, and
 - applying a reinforcing layer on the adhesive layer;wherein said substrate, adhesive layer and reinforcing layer are as defined in either of claims 1 to 13, and the coating amount of the silicone adhesive layer is less than 45 wt%, preferably less than 35 wt%, more preferably less than 20 wt%, based on the total coating amount of the silicone adhesive layer and the reinforcing layer.
 15. Use of the method as claimed in claim 14 for reducing TVOC release.

16. Airbags or artificial leathers containing the composite sheet as defined in one of claims 1 to 13.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2018/123975

A. CLASSIFICATION OF SUBJECT MATTER		
C09J 183/04(2006.01)i; C09D 183/04(2006.01)i; C09D 183/04(2006.01)i; C08L 83/04(2006.01)i; B32B 5/02(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) C09J, C09D, C08L, 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) CNABS,CNTXT, EPODOC, DWPI,ISI Web of Science, Patentics,CNKI:+silicon , +silicone , +siloxane, bilayer? , (second w layer), +vinyl+ , +alkenyl+, +hydrogen+		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 105696361 A (HUIZHOU SAILILONG NEW MAT CO LTD) 22 June 2016 (2016-06-22) claims, description paragraphs 0005-0049, example 1	1-15
X	CN 101443512 A (LUESTAR SILICONES FRANC) 27 May 2009 (2009-05-27) description page 2 the last two paragraphs to page 5 line 5, page 9 line 4 to page 10 line 17, page 12 line 29-page 14 line 16	1-15
X	WO 2016207498 A1 (BLUESTAR SILICONES FRANCE) 29 December 2016 (2016-12-29) claims, examples	1-15
X	JP 03106977 A (SIEGEL KK) 07 May 1991 (1991-05-07) claims, examples	1-15
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<input checked="" 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 07 March 2019		Date of mailing of the international search report 22 March 2019
Name and mailing address of the ISA/CN National Intellectual Property Administration, PRC 6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088 China		Authorized officer YAN,Laiyan
Facsimile No. (86-10)62019451		Telephone No. 86-010-62084471

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2018/123975

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 101535429 A (BLUESTAR SILICONES FRANCE) 16 September 2009 (2009-09-16) the whole document	1-15
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Information on patent family members

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