



(51) International Patent Classification:

C09D 183/05 (2006.01) C09D 183/07 (2006.01)

(21) International Application Number:

PCT/CN2019/098274

(22) International Filing Date:

30 July 2019 (30.07.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(71) Applicant: **DOW SILICONES CORPORATION**

[US/US]; 2200 West Salzburg Road, Midland, Michigan 48686-0994 (US).

(72) Inventors; and

(71) Applicants (for SC only): **WANG, Rui** [CN/CN]; No. 936 Zhangheng Road, Zhangjiang Hi-Tech Park, Pudong District, Shanghai 201203 (CN). **ZHANG, Zhihai** [CN/CN]; No. 936 Zhangheng Road, Zhangjiang Hi-Tech Park, Pudong District, Shanghai 201203 (CN). **FISHER, Mark** [US/US]; 2651 Salzburg Road, 2202 Building, Midland, Michigan 48640 (US). **WANG, Shaohui** [CN/CN]; Room 702, Building 41, No. 748 Of Baochun Road, Minhang District, Shanghai 201100 (CN). **CHEN, Yusheng** [CN/CN]; No. 936 Zhangheng Road, Zhangjiang Hi-Tech Park, Pudong District, Shanghai 201203 (CN).

(74) Agent: **SHANGHAI PATENT & TRADEMARK LAW OFFICE, LLC**; 435 Guiping Road, Shanghai 200233 (CN).

(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))

(54) Title: SILICONE COATINGS FOR AIR BAGS

(57) Abstract: Provided is a hydrosilylation curable textile coating composition comprising: a) a linear organopolysiloxane polymer having at least two alkenyl and/or alkynyl groups per molecule; b) reinforcing fillers comprising fumed silica, precipitated silica and/or calcium carbonate; c) a cross-linker containing at least two silicon bonded hydrogen groups per molecule, alternatively at least three silicon bonded hydrogen groups per molecule selected from one or more of C-1 a trimethyl or dimethyl hydrogen terminated polydimethyl methylhydrogen methylsilsesquioxane siloxane; C-2 a trimethyl or dimethyl hydrogen terminated polymethyl hydrogen siloxane; C-3 a dimethyl hydrogen terminated polydimethyl methylhydrogen siloxane; C-4 an organosilicon resin; C-5 a cyclic siloxane; wherein the molar ratio of silicon bonded hydrogen groups to alkenyl groups and alkynyl groups in the composition is from 1: 1 to 5: 1; d) a hydrosilylation cure catalyst; e) an organosilicon resin containing M and Q units and optionally M<sub>vi</sub> units, f) an adhesion promoter comprising a mixture and/or reaction product of i) one or more alkoxy silanes having an epoxy group in the molecule; ii) a linear organopolysiloxane oligomer containing at least one alkenyl group and at least one hydroxy or alkoxy group per molecule; and iii) an organometallic condensation reaction catalyst comprising organoaluminum or organozirconium compounds. Also provided are a method of coating a textile with the hydrosilylation curable textile coating composition, and an airbag fabric coated therewith.



### **SILICONE COATINGS FOR AIR BAGS**

**[0001]** This disclosure relates to hydrosilylation curable silicone compositions designed to be coated on textiles, in particular airbags and/or airbag fabrics; airbags and/or air bag fabrics coated with a cured product of hydrosilylation curable silicone rubber compositions and to a process for coating air bags and air bag fabrics with the hydrosilylation curable  
5 silicone rubber compositions. The composition has been designed such that in use it will release a low level of volatiles.

**[0002]** Vehicle manufacturers are seeking to reduce the total volatile organic compound (TVOC) content within vehicles. Several interior parts of a vehicle, e.g., interior trim  
10 components, such as seats, panels, and the like are known to release volatile organic compounds (VOCs) and there is a need to minimise these releases. These interior parts can include interior trim components, such as seats, panels, and the like. One internal part which may release VOCs are airbags and it is the intention of this disclosure to provide a hydrosilylation curable silicone composition to minimise the release of volatiles from the  
15 coating itself and/or the airbag onto which it is coated.

**[0003]** Volatile organic compounds (VOCs) are organic chemicals that have a high vapor pressure at ordinary room temperature. Their high vapor pressure results from a low boiling point, e.g., <250° C at atmospheric pressure which causes large numbers of molecules to evaporate or sublime from in the case said parts enter the surrounding air. The Total  
20 Volatile Organic Compound (TVOC) level is a measurement of the sum of all the volatile organic compounds (VOC's) found in an air sample e.g., in a vehicle it is an indication of levels of emissions of organic compounds being given off from non-metallic materials therein.

**[0004]** An airbag generally consists of a textile bag (sometimes referred to as a cushion), a sensor and a means of inflation. When the sensor detects a collision, the inflator causes an  
25 effectively immediate inflation of the airbag, typically by the release of gases. The Air bags and/or airbag fabrics may be made from a woven or knitted fabric made of synthetic fibre, for example of polyamide such as nylon-6,6 or polyester. They may be made from flat fabric pieces which are coated and then sewn together to provide sufficient mechanical strength or may be woven in one piece with integrally woven seams. Sewn air bags are generally  
30 assembled with the coated fabric surface at the inside of the air bag. One-piece woven air bags are coated on the outside of the air bag.

[0005] Today, airbags are standard accessories in most modern vehicles and many of them are coated with a silicone coating which is designed to keep the airbags flexible and resistant to temperature fluctuations, aging and abrasion. They need such properties because, for example, an airbag may remain unused for a long period of time before a collision triggers deployment. This requires the silicone coating to be very stable over time in order to prevent the airbag from becoming stuck and to ensure smooth deployment even after many years. Furthermore, they need good thermal stability given the inflator is usually designed to release extremely hot gases during inflation which could otherwise cause burns to the passenger and prevents or at least significantly reduces the likelihood of the fabric onto which the coating is coated from burning through to the passenger.

[0006] Today in an increasingly safety conscious environment, vehicle manufacturers provide vehicles with an assortment of airbags to improve the protection of vehicle passengers. These may include, but are not restricted to frontal airbags, side airbags, thorax airbags, side curtain airbags and/or knee airbags. Given this propensity to provide several airbags in any one vehicle VOCs might be released and as such silicone coating compositions which minimise this prospect are desired.

[0007] There is provided herein a hydrosilylation curable textile coating composition comprising:

- a) a linear organopolysiloxane polymer having at least two alkenyl and/or alkynyl groups per molecule;
- b) reinforcing fillers comprising fumed silica, precipitated silica and/or calcium carbonate;
- c) a cross-linker containing at least two silicon bonded hydrogen groups, alternatively at least three silicon bonded hydrogen groups selected from one or more of
  - C-1 a trimethyl or dimethyl hydrogen terminated polydimethyl methylhydrogen methylsilsequioxane siloxane;
  - C-2 a trimethyl or dimethyl hydrogen terminated polymethyl hydrogen siloxane;
  - C-3 a dimethyl hydrogen terminated polydimethyl methylhydrogen siloxane;
  - C-4 an organosilicon resin;
  - C-5 a cyclic siloxane,

wherein the molar ratio of silicon bonded hydrogen groups to alkenyl groups and alkynyl groups in the composition is from 1 : 1 to 5:1;

- d) a hydrosilylation cure catalyst;
- e) an organosilicon resin containing M and Q units and optionally  $M^{vi}$  units,
- f) an adhesion promoter comprising a mixture and/or reaction product of
- i) one or more alkoxysilanes having an epoxy group in the molecule;
  - 5 ii) a linear organopolysiloxane oligomer containing at least one alkenyl group and at least one hydroxy or alkoxy group per molecule; and
  - iii) an organometallic condensation reaction catalyst comprising organoaluminum or organozirconium compounds.

**[0008]** There is also provided an airbag fabric coated with an elastomeric coating which is a cured product of the hydrosilylation curable textile coating composition as herein described.

In one embodiment the airbag fabric is in the form of an airbag.

**[0009]** There is also provided a method of coating a textile with a hydrosilylation curable textile coating composition comprising:

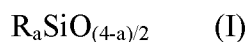
- 15 a) a linear organopolysiloxane polymer having at least two alkenyl and/or alkynyl groups per molecule;
  - b) reinforcing fillers comprising fumed silica, precipitated silica and/or calcium carbonate;
  - c) a cross-linker containing at least two silicon bonded hydrogen groups, alternatively at least three silicon bonded hydrogen groups selected from one or more of
  - 20 C-1 a trimethyl or dimethyl hydrogen terminated polydimethyl methylhydrogen methylsilsesquioxane siloxane;
  - C-2 a trimethyl or dimethyl hydrogen terminated polymethyl hydrogen siloxane;
  - C-3 a dimethyl hydrogen terminated polydimethyl methylhydrogen siloxane;
  - 25 C-4 an organosilicon resin;
  - C-5 a cyclic siloxane,
- wherein the molar ratio of silicon bonded hydrogen groups to alkenyl groups and alkynyl groups in the composition is from 1:1 to 5:1;
- d) a hydrosilylation cure catalyst;
  - 30 e) an organosilicon resin containing M and Q units and optionally  $M^{vi}$  units;
  - f) an adhesion promoter comprising a mixture and/or reaction product of
  - i) one or more alkoxysilanes having an epoxy group in the molecule;

ii) a linear organopolysiloxane oligomer containing at least one alkenyl group and at least one hydroxy or alkoxy group per molecule; and

iii) an organometallic condensation reaction catalyst comprising organoaluminum or organozirconium compounds; by mixing the composition together, coating a textile with the composition and curing the composition on the textile.

**[0010]** There is also provided the use of a composition as hereinbefore described to provide a coated textile with an improved TVOC.

**[0011]** Component (a) of the hydrosilylation curable textile coating composition is one or more polydiorganosiloxane polymer(s) having a viscosity of from 1000 to 500,000mPa.s at 25°C containing at least one alkenyl and/or at least one alkynyl group per molecule, alternatively at least two alkenyl and/or alkynyl groups per molecule, alternatively at least two alkenyl groups per molecule. Polydiorganosiloxane polymer (a) has multiple units of the formula (I):



in which each R is independently selected from an aliphatic hydrocarbyl, aromatic hydrocarbyl, or organyl group (that is any organic substituent group, regardless of functional type, having one free valence at a carbon atom). Saturated aliphatic hydrocarbyls are exemplified by, but not limited to alkyl groups such as methyl, ethyl, propyl, pentyl, octyl, undecyl, and octadecyl and cycloalkyl groups such as cyclohexyl. Unsaturated aliphatic hydrocarbyls are exemplified by, but not limited to, alkenyl groups such as vinyl, allyl, butenyl, pentenyl, cyclohexenyl and hexenyl; and by alkynyl groups. Aromatic hydrocarbon groups are exemplified by, but not limited to, phenyl, tolyl, xylyl, benzyl, styryl, and 2-phenylethyl. Organyl groups are exemplified by, but not limited to, halogenated alkyl groups such as chloromethyl and 3-chloropropyl; nitrogen containing groups such as amino groups, amido groups, imino groups, imido groups; oxygen containing groups such as polyoxyalkylene groups, carbonyl groups, alkoxy groups and hydroxyl groups. Further organyl groups may include sulfur containing groups, phosphorus containing groups and/or boron containing groups. The subscript "a" may be 0, 1, 2 or 3, but is typically mainly 2 or 3.

**[0012]** Examples of typical groups on the polydiorganosiloxane polymer (a) include mainly alkenyl, alkyl, and/or aryl groups. The groups may be in pendent position (on a D or T siloxy unit) or may be terminal (on an M siloxy unit). Hence, suitable alkenyl groups in

polydiorganosiloxane polymer (a) typically contain from 2 to 10 carbon atoms, e.g., vinyl, isopropenyl, allyl, and 5-hexenyl.

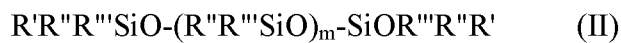
[0013] The silicon-bonded organic groups attached to polydiorganosiloxane polymer (a) other than alkenyl (or alkynyl) groups are typically selected from monovalent saturated hydrocarbon groups, which typically contain from 1 to 10 carbon atoms, and monovalent aromatic hydrocarbon groups, which typically contain from 6 to 12 carbon atoms, which are unsubstituted or substituted with groups that do not interfere with curing of this hydrosilylation curable textile coating composition, such as halogen atoms. Preferred species of the silicon-bonded organic groups are, for example, alkyl groups such as methyl, ethyl, and propyl; and aryl groups such as phenyl.

[0014] The molecular structure of polydiorganosiloxane polymer (a) is typically linear, however, there can be some branching due to the presence of T units (as previously described) within the molecule.

[0015] The viscosity of polydiorganosiloxane polymer (a) should be between 100 and 1000,000mPa.s at 25 °C, alternatively between 1000 and 150,000mPa.s at 25 °C, alternatively, from 1000mPa.s to 125,000mPa.s, alternatively from 1000mPa.s to 50,000mPa.s at 25 °C, measured in accordance with ASTM D1084 using a Brookfield rotational viscometer with the most appropriate spindle for the viscosity being measured at 1 rpm, unless otherwise indicated.

[0016] The polydiorganosiloxane polymer (a) may be selected from polydimethylsiloxanes, alkylmethylpolysiloxanes, alkylarylpolysiloxanes or copolymers thereof containing e.g., alkenyl and/or alkynyl groups and may have any suitable terminal groups, for example, they may be trialkyl terminated, alkenyldialkyl terminated or may be terminated with any other suitable terminal group combination providing each polymer contains at least two alkenyl groups per molecule. Alternatively, polydiorganosiloxane may be partially fluorinated, e.g., it may comprise trifluoroalkyl, e.g., trifluoropropyl groups and or perfluoroalkyl groups. Hence the Polydiorganosiloxane polymer (a) may be, for the sake of example, dimethylvinyl terminated polydimethylsiloxane, dimethylvinylsiloxy-terminated dimethylmethylphenylsiloxane, trialkyl terminated dimethylmethylvinyl polysiloxane or dialkylvinyl terminated dimethylmethylvinyl polysiloxane copolymers.

[0017] For example, a polydiorganosiloxane polymer (a) containing alkenyl groups at the two terminals may be represented by the general formula (II):



**[0018]** In formula (II), each R' may be an alkenyl group or an alkynyl group, which typically contains from 2 to 10 carbon atoms. Alkenyl groups include but are not limited to vinyl, propenyl, butenyl, pentenyl, hexenyl an alkenylated cyclohexyl group, heptenyl, octenyl, nonenyl, decenyl or similar linear and branched alkenyl groups and alkenylated aromatic ringed structures. Alkynyl groups may be selected from but are not limited to ethynyl, propynyl, butynyl, pentynyl, hexynyl an alkynylated cyclohexyl group, heptynyl, octynyl, nonynyl, decynyl or similar linear and branched alkenyl groups and alkenylated aromatic ringed structures.

**[0019]** R'' does not contain ethylenic unsaturation, Each R'' may be the same or different and is individually selected from monovalent saturated hydrocarbon group, which typically contain from 1 to 10 carbon atoms, and monovalent aromatic hydrocarbon group, which typically contain from 6 to 12 carbon atoms. R'' may be unsubstituted or substituted with one or more groups that do not interfere with curing of this hydrosilylation curable textile coating composition, such as halogen atoms. R''' is R' or R''.

**[0020]** The one or more polydiorganosiloxane polymer(s) (a) having a viscosity of from 1000 to 500,000mPa.s at 25°C containing two or more alkenyl groups or alkynyl groups per molecule is present in an amount of from 10 to 90 wt. % of the composition; alternatively, from 40 to 80 wt. % of the of the composition, alternatively from 50 to 75 wt. % of the composition.

**[0021]** Component (b) of the hydrosilylation curable textile coating composition is a reinforcing filler such as fumed silica, precipitated silica and/or calcium carbonate. Finely divided forms of silica are preferred reinforcing fillers (b) e.g., silica fillers having a relatively high surface area, which is typically at least 50 m<sup>2</sup>/g (BET method in accordance with ISO 9277: 2010). For example, fillers, (e.g., fumed silica) having surface areas of from 50-450m<sup>2</sup>/g, alternatively, 50 – 400 450m<sup>2</sup>/g m<sup>2</sup>/g, alternatively from 50 to 300 m<sup>2</sup>/g, alternatively 200 - 300m<sup>2</sup>/g (BET method in accordance with ISO 9277: 2010) are typically used.

**[0022]** When reinforcing filler (b) is naturally hydrophilic (e.g., untreated silica fillers), it is typically treated with a treating agent to render it hydrophobic. These surface modified reinforcing fillers (b) do not clump and can be homogeneously incorporated into polydiorganosiloxane polymer (a), described below, as the surface treatment makes the fillers easily wetted by polydiorganosiloxane polymer (a).

[0023] Typically reinforcing filler (b) may be surface treated with any low molecular weight organosilicon compounds disclosed in the art applicable to prevent creping of organosiloxane compositions during processing. For example, organosilanes, polydiorganosiloxanes, or organosilazanes e.g., hexaalkyl disilazane, short chain siloxane diols or fatty acids or fatty acid esters such as stearates to render the filler(s) hydrophobic and therefore easier to handle and obtain a homogeneous mixture with the other ingredients. Specific examples include but are not restricted to silanol terminated trifluoropropylmethyl siloxane, silanol terminated ViMe siloxane, tetramethyldi(trifluoropropyl)disilazane, tetramethyldivinyl disilazane, silanol terminated MePh siloxane, liquid hydroxyl-terminated polydiorganosiloxane containing an average from 2 to 20 repeating units of diorganosiloxane in each molecule, hexaorganodisiloxane, hexaorganodisilazane. A small amount of water can be added together with the silica treating agent(s) as a processing aid.

[0024] The surface treatment may be undertaken prior to introduction in the hydrosilylation curable textile coating composition or in situ (i.e., in the presence of at least a portion of the other ingredients of the hydrosilylation curable textile coating composition herein by blending these ingredients together at room temperature or above until the filler is completely treated. Typically, untreated reinforcing filler (b) is treated in situ with a treating agent in the presence of polydiorganosiloxane polymer (a) which results in the preparation of a silicone rubber base material which can subsequently be mixed with other ingredients.

[0025] Reinforcing filler is present in an amount of from 1.0 to 50wt. % of the composition, alternatively of from 1 to 30wt. % of the composition, alternatively of from 5.0 to 25wt. % based on the weight % of the composition.

[0026] Cross-linker (c) of the hydrosilylation curable textile coating composition is a linear organopolysiloxane, cyclic organopolysiloxane or organosilicon resin, in each case containing at least two silicon bonded hydrogen groups, alternatively at least three silicon bonded hydrogen groups, selected from one or more of

C-1 a trimethyl or dimethyl hydrogen terminated polydimethyl methylhydrogen methylsilsesquioxane siloxane;

C-2 a trimethyl or dimethyl hydrogen terminated polymethyl hydrogen siloxane;

C-3 a dimethyl hydrogen terminated polydimethyl methylhydrogen siloxane;

C-4 an organosilicon resin; and/or

C-5 a cyclic siloxane.

[0027] Cross-linker (c) of the hydrosilylation curable textile coating composition is used to cross-link polymer (a) through an addition/hydrosilylation reaction of the silicon-bonded hydrogen atoms in said cross-linker (c) with the alkenyl groups and/or alkynyl groups, typically alkenyl groups in polymer (a) catalysed by catalyst (d) described below. The composition is also required to have a molar ratio of silicon bonded hydrogen groups to alkenyl groups and alkynyl groups in the composition of from 1:1 to 5:1, alternatively from 1:1 to 3:1. The cross-linkers C1 to C5 are different from the generally used cross-linker which is different from the standard linear trimethyl terminated polydimethyl methylhydrogen siloxane.

[0028] Each cross-linker (c) normally contains 3 or more silicon-bonded hydrogen atoms so that the hydrogen atoms can react with the unsaturated alkenyl or alkynyl groups of polymer (a) to form a network structure therewith and thereby cure the composition. Some or all of organohydrogenpolysiloxane (c) may alternatively have 2 silicon bonded hydrogen atoms per molecule when polymer (a) has > 2 alkenyl or alkynyl groups per molecule.

[0029] While the molecular weight/viscosity of organohydrogenpolysiloxane (c) is not specifically restricted, the viscosity is typically from 1 to 50,000 mPa.s at 25 °C using a glass capillary viscometer, in order to obtain a good miscibility with polymer (a).

[0030] The silicon-bonded hydrogen (Si-H) content of organohydrogenpolysiloxane (iii) of the hydrosilylation curable silicone elastomer composition is determined using quantitative infra-red analysis in accordance with ASTM E168. In the present instance the silicon-bonded hydrogen to alkenyl (vinyl) and/or alkynyl ratio is important when relying on a hydrosilylation cure process. Generally, this is determined by calculating the total weight % of alkenyl groups in the composition, e.g., vinyl [V] and the total weight % of silicon bonded hydrogen [H] in the composition and given the molecular weight of hydrogen is 1 and of vinyl is 27 the molar ratio of silicon bonded hydrogen to vinyl is  $27[H]/[V]$ . In the composition organohydrogenpolysiloxane (c), the cross-linker, is present in an amount of from 1 to 30 % wt., alternatively 1 to 20 % wt., alternatively 1 to 15 weight.

(d) Hydrosilylation catalyst

[0031] When present hydrosilylation catalyst (d) of the hydrosilylation curable textile coating composition used for application onto the primer treated silicone elastomer substrate is preferably one of the platinum metals (platinum, ruthenium, osmium, rhodium, iridium and palladium), or a compound of one or more of such metals. Platinum and platinum compounds are preferred due to the high activity level of these catalysts in hydrosilylation reactions.

**[0032]** Examples of preferred hydrosilylation catalysts (d) include but are not limited to platinum black, platinum on various solid supports, chloroplatinic acids, alcohol solutions of chloroplatinic acid, and complexes of chloroplatinic acid with ethylenically unsaturated compounds such as olefins and organosiloxanes containing ethylenically unsaturated silicon-bonded hydrocarbon groups. The catalyst (d) can be platinum metal, platinum metal deposited on a carrier, such as silica gel or powdered charcoal, or a compound or complex of a platinum group metal.

**[0033]** Examples of suitable platinum-based catalysts include

(i) complexes of chloroplatinic acid with organosiloxanes containing ethylenically unsaturated hydrocarbon groups are described in US 3,419,593;

(ii) chloroplatinic acid, either in hexahydrate form or anhydrous form;

(iii) a platinum-containing catalyst which is obtained by a method comprising reacting chloroplatinic acid with an aliphatically unsaturated organosilicon compound, such as divinyltetramethyldisiloxane;

(d) alkene-platinum-silyl complexes as described in US Pat. No. 6,605,734 such as (COD)Pt(SiMeCl<sub>2</sub>)<sub>2</sub> where "COD" is 1,5-cyclooctadiene; and/or

(v) Karstedt's catalyst, a platinum divinyl tetramethyl disiloxane complex typically containing about 1 wt. % of platinum in a solvent, such as toluene may be used. These are described in US 3,715,334 and US 3,814,730.

**[0034]** The hydrosilylation catalyst (d) of the hydrosilylation curable textile coating composition is present in the total composition in a catalytic amount, i.e., an amount or quantity sufficient to catalyse the addition/hydrosilylation reaction and cure the composition to an elastomeric material under the desired conditions. Varying levels of the hydrosilylation catalyst (d) can be used to tailor reaction rate and cure kinetics. The catalytic amount of the hydrosilylation catalyst (d) is generally between 0.01 ppm, and 10,000 parts by weight of platinum-group metal, per million parts (ppm), based on the combined weight of the composition polymer (a) and filler (b); alternatively, between 0.01 and 5000ppm; alternatively, between 0.01 and 3,000 ppm, and alternatively between 0.01 and 1,000 ppm. In specific embodiments, the catalytic amount of the catalyst may range from 0.01 to 1,000 ppm, alternatively 0.01 to 750 ppm, alternatively 0.01 to 500 ppm and alternatively 0.01 to 100 ppm of metal based on the weight of the composition. The ranges may relate solely to the metal content within the catalyst or to the catalyst altogether (including its ligands) as specified, but typically these ranges relate solely to

the metal content within the catalyst. The catalyst may be added as a single species or as a mixture of two or more different species. Typically, dependent on the form/concentration in which the catalyst package is provided the amount of catalyst present will be within the range of from 0.001 to 3.0wt. % of the composition.

5 **[0035]** The hydrosilylation curable textile coating composition also comprises component (e) an organosilicon resin containing M and Q units and optionally  $M^{vi}$  units, based on the nomenclature discussed previously. Any suitable MQ resin may be utilised as component (e). Typically, the MQ resins of component (e) comprise  $SiO_{4/2}$  (Q) siloxane units and  $R^2_3 SiO_{1/2}$  (M) siloxane units wherein each  $R^2$  may be the same or different and denotes a monovalent group selected from hydrocarbon groups, preferably having less than 10 20 carbon atoms and, most preferably, having from 1 to 10 carbon atoms. Examples of suitable  $R^2$  groups include alkyl groups, such as methyl, ethyl, propyl, pentyl, octyl, undecyl and octadecyl; cycloaliphatic groups, such as cyclohexyl; aryl groups such as phenyl, tolyl, xylyl, benzyl, alpha-methyl styryl and 2-phenylethyl. Examples of preferred unreactive 15  $R^2_3 SiO_{1/2}$  (M) siloxane units include  $Me_3 SiO_{1/2}$ ,  $PhMe_2 SiO_{1/2}$  and  $Ph_2 MeSiO_{1/2}$ , where Me hereinafter denotes methyl and Ph hereinafter denotes phenyl. Optionally the M type siloxane units may contain alkenyl groups in which case they are denoted as  $M^{vi}$  groups. Usually the alkenyl group is a vinyl group, but other alkenyl groups may alternatively be present. Examples of  $M^{vi}$  groups include but are not limited to  $ViMe_2 SiO_{1/2}$ , 20  $ViPh_2 SiO_{1/2}$ ,  $Vi_2MeSiO_{1/2}$ ,  $Vi_2PhSiO_{1/2}$  groups. The molar ratio of  $M + M^{vi}$  siloxane units to  $SiO_{4/2}$  siloxane units has a value of from 0.5:1 to 1.2:1, alternatively 0.6:1 to 1.1:1.

**[0036]** In one embodiment MQ resin (e) includes a resinous portion wherein the M and/or  $M^{vi}$  units are bonded to  $SiO_{4/2}$  siloxane units (i.e., Q units) and each of Q units is bonded to at least one other  $SiO_{4/2}$  siloxane unit. The molar ratio of M units to Q units is 25 from 0.5 : 1 to 1.2 : 1, alternatively 0.6:1 to 1.1:1, and the resin contains an average of from 1.5 to 7.5 weight% of alkenyl groups, alternatively from about 2 to 5 wt. % of alkenyl groups. The alkenyl and/or alkynyl content is determined using quantitative infra-red analysis in accordance with ASTM E168. The MQ resin (e) may have a number-average molecular weight ( $M_n$ ) of from 2000 to 50,000g/mol, alternatively from 3,000 to 30,000 g/mol. 30 Synthetic polymers and resins invariably consist of a mixture of macromolecular species with different degrees of polymerization and therefore of different molecular weights. There are different types of average polymer molecular weight, which can be measured in different

experiments. The two most important are the number average molecular weight ( $M_n$ ) and the weight average molecular weight ( $M_w$ ). The  $M_n$  and  $M_w$  of a silicone polymer and/or resin can be determined by Gel permeation chromatography (GPC) with precision of about 10-15%. This technique is standard and yields  $M_w$ ,  $M_n$  and polydispersity index (PI). The degree of polymerisation (DP) =  $M_n/M_u$  where  $M_n$  is the number-average molecular weight coming from the GPC measurement and  $M_u$  is the molecular weight of a monomer unit.  $PI = M_w/M_n$ . The DP is linked to the viscosity of the polymer via  $M_w$ , the higher the DP, the higher the viscosity.

**[0037]** The MQ resin (e) may be present in the composition in an amount of from 1-60% wt., alternatively 1-40% wt., and is preferably in the form of either an MQ or an MM<sup>vi</sup>Q resin.

**[0038]** The hydrosilylation curable textile coating composition herein also comprises an adhesion promoter (f) comprising a mixture and/or reaction product of:

i) one or more alkoxy silanes having an epoxy group in the molecule;

(ii) a linear organopolysiloxane oligomer containing at least one alkenyl group and at least one hydroxy or alkoxy group per molecule; and

(iii) an organometallic condensation reaction catalyst comprising organoaluminum or organozirconium compounds.

**[0039]** The first component of the adhesion promoter (f) (i) is an epoxy-containing alkoxy silane. Examples of epoxy-containing alkoxy silanes may include 3-glycidoxypropyl trimethoxysilane, 3-glycidoxypropyl triethoxysilane, 3-glycidoxypropyl methyl dimethoxysilane, 4-glycidoxybutyl trimethoxysilane, 5,6-epoxyhexyl triethoxysilane, 2-(3,4-epoxycyclohexyl) ethyl trimethoxysilane, or 2-(3,4-epoxycyclohexyl)

ethyl triethoxysilane. Component (f)(i) may be present in the composition in an amount of from 0.1 to 5% by weight of the composition, alternatively 0.5 to 3% by weight, alternatively 0.5 to 2% by weight of the composition.

**[0040]** The second component of the adhesion promoter (f)(ii) is an organopolysiloxane oligomer containing at least one alkenyl and at least one hydroxy or alkoxy group in the molecule, for example an  $\alpha$ ,  $\omega$ -hydroxy or alkoxy or both groups terminated polysiloxane containing pendant alkenyl groups in the molecule.

**[0041]** The oligomeric organopolysiloxane can for example be a methylvinyl polysiloxane in which both molecular terminals are dimethylhydroxysiloxy units, or a copolymer of a methylvinyl siloxane and dimethylsiloxane units in which both molecular terminals are

dimethylhydroxysiloxy units. The oligomeric organopolysiloxane can be a mixture of organopolysiloxane molecules, some of which have silanol end groups at both molecular terminals and some of which have only one silanol group such as a dimethylhydroxysiloxy terminal unit with the other terminal unit being for example a dimethylmethoxysiloxy unit, a trimethylsiloxy unit or a dimethylvinylsiloxy unit. Preferably more than 50% by weight of the oligomeric organopolysiloxane, more preferably 60-100% comprises molecules having silanol end groups at both molecular terminals.

**[0042]** The oligomeric organopolysiloxane preferably contains at least 3%, more preferably at least 5%, by weight vinyl groups, and can contain up to 35 or 40% by weight vinyl groups. Most preferably the oligomeric organopolysiloxane contains 5 to 30% by weight vinyl groups. The oligomeric organopolysiloxane preferably has a molecular weight of 1000 to 10000. The oligomeric organopolysiloxane preferably has a viscosity of from 0.1 to 300 mPa.s, alternatively a viscosity of 0.1 to 200 mPa.s, alternatively from 1 to 100 mPa.s. (measured using a Brookfield DV 3T Rheometer at 25°C). Component (f)(ii) may be present in the composition in an amount of from 0.1 to 5% by weight of the composition, alternatively 0.1 to 3% by weight, alternatively 0.1 to 2% by weight of the composition.

**[0043]** The third part of the adhesion promoter (f)(iii) is a suitable condensation catalyst which may be used to catalyse the reaction of the other components of the adhesion promoter, namely (f)(i) and (ii) and comprises a zirconate and/or aluminate condensation catalysts used to activate and/or accelerate the reaction of the adhesion promoter (f) described above. The condensation catalyst may be selected from organometallic catalyst comprising zirconates, organoaluminium chelates, and/or zirconium chelates.

**[0044]** Zirconate based catalysts may comprise a compound according to the general formula or  $Zr[OR^5]_4$  where each  $R^5$  may be the same or different and represents a monovalent, primary, secondary or tertiary aliphatic hydrocarbon group which may be linear or branched containing from 1 to 20 carbon atoms, alternatively 1 to 10 carbon atoms. Optionally the zirconate may contain partially unsaturated groups. Preferred examples of  $R^5$  include but are not restricted to methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl and a branched secondary alkyl group such as 2,4-dimethyl-3-pentyl. Preferably, when each  $R^5$  is the same,  $R^5$  is an isopropyl, branched secondary alkyl group or a tertiary alkyl group, in particular, tertiary butyl. Specific examples include, zirconium tetrapropylate and zirconium tetrabutylate, tetra-isopropyl zirconate, zirconium (IV) tetraacetyl acetate, (sometimes

referred to as zirconium AcAc<sub>4</sub>, zirconium (IV) hexafluoroacetyl acetonate, zirconium (IV) trifluoroacetyl acetonate, tetrakis (ethyltrifluoroacetyl acetonate) zirconium, tetrakis (2,2,6,6-tetramethyl-heptanethionate) zirconium, zirconium (IV) dibutoxy bis(ethylacetonate), zirconium tributoxyacetylacetate, zirconium butoxyacetylacetate bisethylacetoacetate, zirconium butoxyacetylacetate bisethylacetoacetate, diisopropoxy bis (2,2,6,6-tetramethyl-heptanethionate) zirconium, or similar zirconium complexes having β-diketones (including alkyl-substituted and fluoro-substituted forms thereof) which are used as ligands.

**[0045]** Suitable aluminum based condensation catalysts may include but are not limited to one or more of Al(OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub>, Al(OC<sub>3</sub>H<sub>7</sub>)<sub>2</sub>(C<sub>3</sub>COCH<sub>2</sub>COC<sub>12</sub>H<sub>25</sub>), Al(OC<sub>3</sub>H<sub>7</sub>)<sub>2</sub>(OCOCH<sub>3</sub>), and Al(OC<sub>3</sub>H<sub>7</sub>)<sub>2</sub>(OCOC<sub>12</sub>H<sub>25</sub>).

**[0046]** Component (f)(iii) may be present in the composition in an amount of from 0.1 to 5% by weight of the composition, alternatively 0.1 to 3% by weight, alternatively 0.1 to 2% by weight of the composition.

**[0047]** The adhesion promoter (f) is typically present in the composition in a cumulative amount of (f)(i),(ii) and (iii) of from about 0.3 to 6% wt. of the composition; alternatively, 0.3 to 4 % wt. of the composition.

**[0048]** When the hydrosilylation curable textile coating composition as hereinbefore described is being cured via an addition/hydrosilylation reaction an inhibitor may be utilised to inhibit the cure of the composition. These inhibitors are utilised to prevent premature cure in storage and/or to obtain a longer working time or pot life of a hydrosilylation cured composition by retarding or suppressing the activity of the catalyst. Inhibitors of hydrosilylation catalysts (d), e.g., platinum metal-based catalysts are well known in the art and may include hydrazines, triazoles, phosphines, mercaptans, organic nitrogen compounds, acetylenic alcohols, silylated acetylenic alcohols, maleates, such as dibutyl maleate; fumarates, ethylenically or aromatically unsaturated amides, ethylenically unsaturated isocyanates, olefinic siloxanes, such as tetramethyltetravinylcyclotetrasiloxane; unsaturated hydrocarbon monoesters and diesters, conjugated ene-yne, hydroperoxides, nitriles, and diaziridines. Alkenyl-substituted siloxanes as described in US 3,989,667 may be used, of which cyclic methylvinylsiloxanes are preferred.

**[0049]** One class of known inhibitors of hydrosilylation catalysts, e.g., platinum catalysts (d) includes the acetylenic compounds disclosed in US 3,445,420. Acetylenic alcohols such as 2-methyl-3-butyn-2-ol constitute a preferred class of inhibitors that will suppress the activity of a

platinum-containing catalyst at 25 °C. Compositions containing these inhibitors typically require heating at temperature of 70 °C or above to cure at a practical rate.

**[0050]** Examples of acetylenic alcohols and their derivatives include 1-ethynyl-1-cyclohexanol (ETCH), 2-methyl-3-butyn-2-ol, 3-butyn-1-ol, 3-methyl butynol 3-butyn-2-ol, propargyl alcohol, 2-phenyl-2-propyn-1-ol, 3,5-dimethyl-1-hexyn-3-ol, 1-ethynylcyclopentanol, 1-phenyl-2-propynol, 3-methyl-1-penten-4-yn-3-ol, and mixtures thereof. In one alternative the inhibitor is selected from one or more of 1-ethynyl-1-cyclohexanol (ETCH), tetramethyltetravinylcyclotetrasiloxane, 3-methyl butynol and/or dibutyl maleate.

**[0051]** When present, inhibitor concentrations as low as 1 mole of inhibitor per mole of the metal of catalyst (d) will in some instances impart satisfactory storage stability and cure rate. In other instances, inhibitor concentrations of up to 500 moles of inhibitor per mole of the metal of catalyst (d) are required. The optimum concentration for a given inhibitor in a given hydrosilylation curable textile coating composition herein is readily determined by routine experimentation. Mixtures of the above may also be used. Dependent on the concentration and form in which the inhibitor selected is provided/available commercially, when present in the composition, the inhibitor is typically present in an amount of from 0.0001-10% wt., alternatively 0.001-5%, inhibitor, alternatively 0.0125 to 5wt. % of the composition.

#### **Additional optional ingredients**

**[0052]** Additional optional ingredients may be present in the liquid silicone rubber composition as hereinbefore described depending on the intended final use thereof. Examples of such optional ingredients include thermally conductive fillers, pot life extenders, flame retardants, lubricants, non-reinforcing fillers, pigments and/or colouring agents, bactericides, wetting agent, heat stabilizer, compression set additive, plasticizer, and mixtures thereof.

**[0053]** Pot life extenders, such as triazole, may be used, but are not considered necessary in the scope of the present invention. The liquid curable silicone rubber composition may thus be free of pot life extender.

**[0054]** Examples of flame retardants include aluminium trihydrate, chlorinated paraffins, hexabromocyclododecane, triphenyl phosphate, dimethyl methylphosphonate, tris(2,3-dibromopropyl) phosphate (brominated tris), and mixtures or derivatives thereof.

**[0055]** Examples of lubricants include tetrafluoroethylene, resin powder, graphite, fluorinated graphite, talc, boron nitride, fluorine oil, silicone oil, molybdenum disulfide, and

mixtures or derivatives thereof. When present in the composition, flame retardants are typically present in an amount of from 0.1 to 5% by weight of the composition.

**[0056]** Non-reinforcing fillers may include such as crushed quartz, diatomaceous earths, barium sulphate, iron oxide, titanium dioxide and carbon black, talc, wollastonite. Other fillers which might be used alone or in addition to the above include aluminite, calcium sulphate (anhydrite), gypsum, calcium sulphate, magnesium carbonate, clays such as kaolin, aluminium trihydroxide, magnesium hydroxide e.g., brucite, graphite, copper carbonate, e.g., malachite, nickel carbonate, e.g., zarachite, barium carbonate, e.g., witherite and/or strontium carbonate e.g., strontianite.

**[0057]** Other fillers may include, aluminium oxide, silicates from the group consisting of olivine group; garnet group; aluminosilicates; ring silicates; chain silicates; and sheet silicates. The olivine group comprises silicate minerals, such as but not limited to, forsterite and  $Mg_2SiO_4$ . The garnet group comprises ground silicate minerals, such as but not limited to, pyrope;  $Mg_3Al_2Si_3O_{12}$ ; grossular; and  $Ca_2Al_2Si_3O_{12}$ . Aluminosilicates comprise ground silicate minerals, such as but not limited to, sillimanite;  $Al_2SiO_5$ ; mullite;  $3Al_2O_3 \cdot 2SiO_2$ ; kyanite; and  $Al_2SiO_5$ . Ring silicates may be utilised as non-reinforcing fillers, these include silicate minerals, such as but not limited to, cordierite and  $Al_3(Mg,Fe)_2[Si_4AlO_{18}]$ . The chain silicates group comprises ground silicate minerals, such as but not limited to, wollastonite and  $Ca[SiO_3]$ . Sheet silicates may alternatively or additionally be used as non-reinforcing fillers where appropriate group comprises silicate minerals, such as but not limited to, mica;  $K_2Al_4[Si_6Al_2O_{20}](OH)_4$ ; pyrophyllite;  $Al_4[Si_8O_{20}](OH)_4$ ; talc;  $Mg_6[Si_8O_{20}](OH)_4$ ; serpentine for example, asbestos; Kaolinite;  $Al_4[Si_4O_{10}](OH)_8$ ; and vermiculite. In one alternative the fillers will be selected from one or more of fumed silica, precipitated silica, calcium carbonate, talc, mica, quartz and, aluminium oxide.

**[0058]** Further additives include silicone fluids, such as trimethylsilyl or OH terminated siloxanes. Such trimethylsiloxy or OH terminated polydimethylsiloxanes typically have a viscosity  $< 150$  mPa.s at  $25^\circ C$  measured using a Brookfield DV 3T Rheometer. When present such silicone fluid may be present in the liquid curable silicone rubber composition in an amount ranging of from 0.1 to 5% by weight (% wt.), based on the total weight of the composition and may function as mold release agents.

**[0059]** Examples of pigments include titanium dioxide, chromium oxide, bismuth vanadium oxide, iron oxides and mixtures thereof.

[0060] Examples of colouring agents for textile coating include pigments, vat dyes, reactive dyes, acid dyes, chrome dyes, disperse dyes, cationic dyes and mixtures thereof.

[0061] In a preferred embodiment of the invention, the pigments and dyes are used in form of pigment masterbatch composed of them dispersed in the polydiorganosiloxane with a low viscosity (ingredient (a)) at the ratio of 25:75 to 70:30.

[0062] Examples of heat stabilizers include metal compounds such as red iron oxide, yellow iron oxide, ferric hydroxide, cerium oxide, cerium hydroxide, lanthanum oxide, copper phthalocyanine, aluminum hydroxide, fumed titanium dioxide, iron naphthenate, cerium naphthenate, cerium dimethylpolysilanolate and acetylacetone salts of a metal chosen from copper, zinc, aluminum, iron, cerium, zirconium, titanium and the like. The amount of heat stabilizer when present in a composition may range from 0.01 to 1.0 % weight of the total composition.

[0063] In one embodiment there is provided a hydrosilylation curable textile coating composition comprising:

- a) a linear organopolysiloxane polymer of polydiorganosiloxane polymer (a) having a viscosity of from 100 and 1000,000mPa.s at 25 °C, alternatively between 1000 and 150,000mPa.s at 25 °C, alternatively from 1000mPa.s to 125,000mPa.s, alternatively from 1000mPa.s to 50,000mPa.s at 25 °C having at least two alkenyl and/or alkynyl groups per molecule in an amount of from 10 to 90 wt. wt. % of the of the composition; alternatively, from 40 to 80 wt. % of the of the composition, alternatively from 50 to 75 wt. of the composition;
- b) reinforcing fillers comprising fumed silica, precipitated silica and/or calcium carbonate in an amount of from 1.0 to 50wt. % of the composition, alternatively of from 1 to 30wt. % of the solids content of the composition, alternatively of from 5.0 to 25wt. % based on the weight % of the solids content of the composition.
- c) a cross-linker containing at least two silicon bonded hydrogen (Si-H) groups, alternatively at least three Si-H groups in an amount of from 1 to 30 % wt., alternatively 1 to 20 % wt., alternatively 1 to 15 weight, selected from one or more of
- C-1 a trimethyl or dimethyl hydrogen terminated polydimethyl methylhydrogen methylsilsequioxane siloxane;
- C-2 a trimethyl or dimethyl hydrogen terminated polymethyl hydrogen siloxane;
- C-3 a dimethyl hydrogen terminated polydimethyl methylhydrogen siloxane;

C-4 an organosilicon resin;

C-5 a cyclic siloxane;

wherein the molar ratio of silicon bonded hydrogen groups to alkenyl groups and alkynyl groups in the composition is from 1:1 to 5:1;

- 5 d) a hydrosilylation cure catalyst in an amount of from 0.001 to 3.0wt. % of the composition;  
e) an organosilicon resin containing M and Q units and optionally M<sup>vi</sup> units, in an amount of from 1-60% wt., alternatively 1-40% wt.; of the composition;

f) an adhesion promoter comprising a mixture and/or reaction product of

- i) one or more alkoxysilanes having an epoxy group in the molecule in an  
10 amount of from 0.1 to 5% by weight of the composition, alternatively 0.5 to 3% by weight, alternatively 0.5 to 2% by weight of the composition;

ii) a linear organopolysiloxane oligomer containing at least one alkenyl group and at least one hydroxy or alkoxy group per molecule in an amount of from 0.1 to 5% by weight of the composition, alternatively 0.1 to 3% by weight, alternatively 0.1 to 2% by

15 weight of the composition; and

iii) an organometallic condensation reaction catalyst comprising organoaluminum or organozirconium compounds composition in an amount of from 0.1 to 5% by weight of the composition, alternatively 0.1 to 3% by weight, alternatively 0.1 to 2% by weight of the composition;

20 which adhesion promoter (f) is typically present in the composition in a cumulative amount of (f)(i),(ii) and (iii) of from about 0.3 to 6% wt. of the composition; alternatively, 0.3 to 4 % wt. of the composition. The composition may be any combination of the above ranges providing the total wt. % is 100 wt. %.

**[0064]** Typically prior to use the composition is stored in two parts, Part A and part B to  
25 keep ingredients (b) and (d) apart to avoid premature cure. Typically, a Part A composition will comprise components (a), (c) and (d) and Part B will comprise components (a), (b) and (c) and inhibitor when present. Component (e) above may be present in either or both Part A and Part B. Regarding the adhesion promoter, to prevent premature reaction, component f) (iii) is usually stored in part A and components f) (i) and (ii) are stored in part B.

30 **[0065]** Additives when present in the composition may be in either Part A or Part B providing they do not negatively affect the properties of any other ingredient (e.g., catalyst inactivation). Part A and part B of the hydrosilylation curable textile coating composition

described herein are mixed together shortly prior to use to initiate cure of the full composition into a silicone elastomeric material. The compositions can be designed to be mixed in any suitable ratio e.g., part A : part B may be mixed together in ratios of from 10:1 to 1:10, alternatively from 5:1 to 1:5, alternatively from 2:1 to 1:2, but most preferred is a ratio of 1:1.

5 **[0066]** Ingredients in each of Part A and/or Part B may be mixed together individually or may be introduced into the composition in pre-prepared combinations for, e.g., ease of mixing the final composition. For Example, components (a) and (b) are often mixed together to form an LSR polymer base or masterbatch prior to addition with other ingredients. These may then be mixed with the other ingredients of the Part being made directly or may  
10 be used to make pre-prepared concentrates commonly referred to in the industry as masterbatches.

**[0067]** In this instance, for ease of mixing ingredients, one or more masterbatches may be utilised to successfully mix the ingredients to form Part A and/or Part B compositions. For example, a “fumed silica” masterbatch may be prepared. This is effectively an LSR  
15 silicone rubber base with silica treated in situ. Any suitable additive may be incorporated into such a composition to form a concentrate /masterbatch to improve ease of introduction.

Table. 1 Fumed Silica Masterbatch

	Preferred
Fumed Silica having a surface area of from 50-450m <sup>2</sup> /g, alternatively, 50 – 400 m <sup>2</sup> /g, alternatively from 50 to 300 m <sup>2</sup> /g, alternatively 200 - 300m <sup>2</sup> /g (BET method in accordance with ISO 9277: 2010)	20-30%
Dimethylvinyl terminated polydimethylsiloxane having a viscosity of from 1000 to 100,000mPa.s at 25°C	60-70%
Hexamethyldisilazane	2-10%
Tetramethyldivinyl disilazane	0-1%
Dimethylhydroxy terminated vinylmethyl polysiloxane or a Dimethylhydroxy terminated vinylmethyl dimethyl polysiloxane having a viscosity of from 5 to 500mPa.s and a vinyl content of 10 to 15 % wt.	0-1%
Water	0.5-5%

**[0068]** Hence, if a fumed silica masterbatch were utilised the Part A and part B compositions for a two-part composition to be mixed in a 1:1 weight ratio might be depicted in the following Table 2.

Table 2 LSR part A&B formulation:

	PART A	PART B
Fumed Silica Masterbatch from Table 1 above	20-80%	20-80%
Silicone Resin polymer (10 to 60% by weight of the mixture being silicone resin and 40 to 90% by weight being organopolysiloxane (a))	1-70%	1-70%
dimethylvinyl-terminated polydimethylsiloxane having a viscosity of from 1000 to 100,000mPa.s at 25°C	0-50%	0-50%
Cross-linker		1.0-20.0%
Platinum catalyst solution	0.01-3.0%	
Cure inhibitor (if present)		0.0001-5.0%

5 **[0069]** The composition would also comprise 0.3 to 6% wt. of adhesion promoter with adhesion catalyst in Part A and the other components of the adhesion promoter in Part B. In each instance the total composition in Table 2 for part A and Part B compositions are 100% respectively.

10 **[0070]** Parts A and B of the composition may be prepared by combining all of their respective ingredients at ambient temperature. Any mixing techniques and devices described in the prior art can be used for this purpose. The particular device to be used will be determined by the viscosities of ingredients and the final composition. Suitable mixers include but are not limited to paddle type mixers e.g., planetary mixers and kneader type mixers. Cooling of ingredients during mixing may be desirable to avoid premature curing  
15 of the composition.

**[0071]** Prior to use the respective Part A and Part B compositions are mixed together in the desired ratio.

20 **[0072]** The present disclosure includes a process for coating a fabric with the coating composition as hereinbefore described. The fabric is preferably a woven fabric, particularly a plain weave fabric, but can for example be a knitted or nonwoven fabric. The fabric may be made from synthetic fibres or blends of natural and synthetic fibres, for example polyamide fibres such as nylon-6,6, polyester, polyimide, polyethylene, polypropylene,

polyester-cotton, or glass fibres. For use as air bag fabric, the fabric should be sufficiently flexible to be able to be folded into relatively small volumes, but also sufficiently strong to withstand deployment at high speed, e.g., under the influence of an explosive charge. The coating compositions as hereinbefore described have good adhesion to plain weave nylon and polyester fabrics, which are generally difficult to adhere to. The coating compositions as  
5 hereinbefore described have particularly good adhesion and film forming properties immediately on contacting the fabric, so that film formation on the surface of the fabric being coated is uniform. The coating compositions of the invention also have good penetration into the fabric. Coated fabrics as hereinbefore described reduce gas permeability and/or good air  
10 tightness.

**[0073]** The coating composition as hereinbefore described may be applied on to the fabric substrate by any suitable known technique. These include spraying, gravure coating, bar coating, coating by knife-over-roller, coating by knife-over-air, padding, dipping and screen-printing. The coating composition can be applied to an air bag fabric which is to be cut into  
15 pieces and sewn to assemble an air bag, or to a one-piece woven air bag. The coating composition is generally applied at a coat-weight of at least  $10 \text{ g/m}^2$ , alternatively at least  $15 \text{ g/m}^2$ , and may be applied at up to  $100$  or  $150 \text{ g/m}^2$ , if required.

**[0074]** Although it is not preferred, it is possible to apply the composition in multiple layers, which together have the coat weights set out above. It is also possible to apply onto the  
20 coating composition a further compatible coating, e.g., of a material providing e.g., low friction, if deemed necessary.

**[0075]** Whilst the coating compositions as hereinbefore described are capable of curing at ambient temperature over prolonged periods, it is preferred that curing conditions for the coating composition are at elevated temperatures over a period which will vary depending on  
25 the actual temperature used, for example  $120$  to  $200^\circ\text{C}$  for a period of 5 seconds to 5 minutes.

**[0076]** This composition is designed to provide low TVOC/carbon emission ( $<40\text{ppm}$ ) hydrosilylation curable textile coating compositions for coating airbag fabrics and/or  
airbags suitable for the production of low TVOC/carbon emission airbag, to meet original equipment manufacturers (OEMs) emission requirements for non-metallic vehicle interior  
30 materials through the combination of the specific silicon bonded hydrogen containing crosslinkers (C-1 to C-5) in combination with the adhesion promoter. The adhesion promoter provides a strong bonding performance between the resulting coating and the fabric

substrate, including woven fabrics. The coatings produced from the composition herein provide the resulting coated airbags/airbag fabrics with excellent scrub resistance and improved durability after heat humidity aging at 70°C and 95% relative humidity for 408 hours. Resulting coated airbags will therefore provide better reliability better safety protection to driver and passengers in the vehicle. The coated fabric shows low TVOC, low stiffness, good hand feeling, excellent scrub resistance and anti-blocking performance.

[0077] This technology can be used in any suitable airbag application, particularly in the automobile market but also for e.g., escape chutes from aircraft or alternatively as a textile binder coating composition. The fabric substrate onto which the composition as hereinbefore described is applied may be a woven fabric, particularly a plain weave fabric, but can for example be a knitted or nonwoven fabric. The fabric may be made from synthetic fibres or blends of natural and synthetic fibres, for example polyamide fibres such as nylon-6,6, polyester, polyamine polyimide, polyethylene, polypropylene, polyester-cotton, or glass fibres. is preferably a woven fabric, particularly a plain weave fabric, but can for example be a knitted or nonwoven fabric. The preferred fabrics include polyamide and polyester for airbag/textile coating application.

### Examples

[0078] In the following examples, %ages are given in weight unless otherwise stated and all viscosity measurements occur at 25°C unless otherwise indicated. Unless otherwise indicated, the viscosity of the polymers was measured in accordance with ASTM D1084 using a Brookfield rotational viscometer with the most appropriate spindle for the viscosity being measured at 1 rpm, unless otherwise indicated. Cross-linker viscosities were measured using a glass capillary viscometer. Vinyl group and Si-H group content was measured by Infrared spectroscopy in accordance with ASTM E168 using standards of the carbon double bond stretch and silicon-hydrogen bond stretch respectively.

### Preparation process

[0079] As a first step an in-situ treated fumed silica masterbatch was prepared in a Kneader mixer by mixing the ingredients depicted in Table 1 and the stripping off residual water and treatment agents.

Table 1: In-situ treated fumed silica masterbatch ingredients

	Weight %
Fumed silica surface area of about 300m <sup>2</sup> /g (ISO 9277: 2010)	28.15
dimethylvinyl-terminated polydimethylsiloxane (1) having a viscosity of 65,000mPa.s	65.0
Hexamethyldisilazane	5.0
Dimethylhydroxy terminated vinylmethyl dimethyl polysiloxane having a viscosity of about 30mPa.s and a vinyl content of 12.5 % wt.	0.15
Water	1.7

5

**[0080]** The resulting fumed silica masterbatch was then utilised to make the two-part liquid silicone rubber compositions depicted below in the following Tables in which

**Resin/Polymer 1 Mixture:** is a mixture of an organosilicon resin and a dimethylvinyl terminated polydimethylsiloxane polymer. The organosilicon resin has number average molecular weight of about 21,000g/mol (GPC), a molar ratio of M groups to Q groups of about 0.8:1 and a vinyl content of about 5% wt. The polymer has a vinyl content of 0.23% wt., and the mixture contains 34 wt. % resin and has a viscosity of about 6000mPa.s.

**Polymer 1:** Dimethylvinyl terminated polydimethylsiloxane polymer having a vinyl content of 0.14% wt. and a viscosity of 12,000 mPa.s.

**Cross-linker type (C-1):** is a trimethyl terminated polydimethyl methylhydrogen methylsilsesquioxane siloxane having a viscosity of about 15 mPa.s and a silicone bonded hydrogen (Si-H) content of 0.85% wt.

**Cross-linker type (C-2):** trimethyl terminated polymethyl hydrogen siloxane; having a viscosity of about 25 mPa.s and an Si-H content of 1.57% wt.

**Cross-linker type (C-3):** dimethyl hydrogen terminated polydimethyl methylhydrogen siloxane having a viscosity of about 9 mPa.s and a Si-H content of 0.39% wt.

**Cross-linker type (C-4):** an organosilicon resin having a viscosity of about 35 mPa.s and a Si-H content of 0.96% wt.

20

**Cross-linker type (C-5):** cyclic siloxanes having a viscosity of about 1.0mPa.s and a Si-H content of 1.67% wt.

**[0081]** Part A containing Pt catalyst and Part B containing SiH crosslinker, were then mixed in a suitable ratio from 1:100 to 1:1. In the following the composition is designed to be mixed in a 1:1 weight ratio in a Turello mixer.

Table 2: LSR Part A

Formulation	Comp. 1 (wt.%)	Standard (wt.%)
Fumed Silica Masterbatch	31	30
Resin/Polymer 1 Mixture	67.08	30
Polymer 1		38.08
Pt catalyst masterbatch containing 5,000ppm Pt	0.32	0.32
1 : 1 wt. ratio zirconium tetrakisacetylacetonate/Polymer 1 mixture	1.6	1.6

**[0082]** Excepting comp. 1 all other examples and comparatives used the Part A composition indicated as standard in Table 1.

Table 3a: LSR Part B

Formulation	Comp. 1 (wt.%)	Comp. 2 (wt.%)	Ex. 1 (wt.%)	Ex. 2 (wt.%)
Fumed Silica Masterbatch	22	30	30	30
Resin/Polymer 1 Mixture	58.92	30	30	30
Polymer 1		27.42	28.82	33.72
Trimethyl terminated polydimethyl methylhydrogen siloxane, viscosity 5mPa.s and 0.75% wt. Si-H content	16.3	9.8		
Cross-linker type (C-1)			8.4	
Cross-linker type (C-2)				3.5
Ethynyl Cyclohexanol	1.0	1.0	1.0	1.0
Glycidoxypropyltrimethoxysilane	1.42	1.42	1.42	1.42
Dimethylhydroxy terminated vinylmethyl dimethyl polysiloxane having a viscosity of	0.36	0.36	0.36	0.36

about 30mPa.s and vinyl content of 12.5% wt				
---	--	--	--	--

Table 3b: LSR Part B

Formulation	Ex. 3 (wt%)	Ex. 4 (wt%)	Ex. 5 (wt%)
Fumed Silica Masterbatch	30	30	30
Resin/Polymer 1 Mixture	30	30	30
Polymer 1	28.02	28.62	34.02
Cross-linker type (C-3)	9.2		
Cross-linker type (C-4)		7.6	
Cross-linker type (C-5)			3.2
Ethynyl Cyclohexanol	1.0	2.0	1.0
Glycidoxypropyltrimethoxysilane	1.42	1.42	1.42
Dimethylhydroxy terminated vinylmethyl dimethyl polysiloxane having a viscosity of about 30mPa.s and vinyl content of 12.5% wt.	0.36	0.36	0.36

The Si-H to vinyl ratio for all comparatives and examples were in the region of 2.5 to 3:1.

**[0083]** The physical properties of the different examples and comparatives depicted in Tables 2 and 3 above were determined to ensure they were satisfactory. Samples were pressed to a thickness of 2mm, at a temperature of 120°C for 10 minutes. Other physical property testing followed ASTM standard (D2204 for Hardness, D412 for Tensile strength and Elongation at break, D4287 for viscosity, and D624 for tear strength).

10

15

Table 4: Physical properties

	Comp. 1	Comp. 2	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Mixed viscosity 10/s (Pa.s, ASTM D4287)	17	20	22	25	25	26	28
Hardness (Shore A, ASTM D2204)	41	32	33	37	18	36	40
Tensile strength (MPa, ASTM D412)	4.9	4.1	4.5	4.9	3.3	4.1	4.3
Elongation at break (%, ASTM D412)	237	293	335	298	358	279	223
Tear Strength (Die C, KN/m, ASTM D624)	19.3	15.8	16.5	16.5	15.3	17.4	18.7

- 5 **[0084]** Samples of coated fabrics, coated with the example and comparative examples depicted above were prepared using a Mathis lab coater. The Part A and Part B compositions were mixed in a 1:1 weight ratio in a speed mixer with. Then the resulting mixture was coated on PA66 (Nylon 66 woven fabric) and PET (polyethylene terephthalate woven fabric) respectively in the Mathis lab coater by knife coating. The coated fabrics were
- 10 then heated at 190°C for 1min. to cure the coating on the fabric and then subsequent to cooling the coat weight was determined and was found to be approximately  $35\pm 5\text{g/m}^2$  for each sample. The resulting coated fabrics were then tested for TVOC in accordance with VDA277.

Table 5: TVOC of coated fabrics (ppm) ( $\mu\text{g C/g}$ , ppm, VDA 277)

	Comp. 1	Comp. 2	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
lab coated PA66	122	85	37	28	39	32	26
lab coated PET	105	70	36	33	37	34	31
coated PA66	120		26	19			
coated PET	90		20	12			
lab coated PA66	122	85	37	28	39	32	

**[0085]** Comparing with example 1 and 2 with traditional SiH crosslinker, the TVOC of LSR compositions using special SiH crosslinkers was reduced significantly. The application of these special SiH crosslinker is effective to TVOC reduction in examples of the compositions herein and all samples tested gave a TVOC of < 40ppm and in several instances < 30ppm.

**[0086]** Samples of the coated fabrics were also analysed for scrub (abrasion) resistance before and after heat/humidity aging at 70°C and 95% relative humidity for 408 hrs according to EASC 99040180 A09 and the results are shown in Tables 6a and 6b below.

Table 6a: Scrub Resistance (Strokes)

	Comp. 1	Comp. 2	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Coated PA66	1600	2000	2000	2000	1000	1000	1000
Coated PET	1600	2000	2000	2000	1000	1000	1000

Table 6b: Scrub Resistance (strokes) after heat humidity aging

	Comp. 1	Comp. 2	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Coated PA66	1200	1600	1600	1600	600	600	600
Coated PET	1200	1600	1600	1600	600	600	600

**[0087]** Some of the compositions, for example 2, 3 and 4, also shown excellent scrub resistance and high stability after heat/humidity aging (i.e., >600 strokes).

**CLAIMS**

1. A hydrosilylation curable textile coating composition comprising:
- 5 a) a linear organopolysiloxane polymer having at least two alkenyl and/or alkynyl groups per molecule;
- b) reinforcing fillers comprising fumed silica, precipitated silica and/or calcium carbonate;
- c) a cross-linker containing at least two silicon bonded hydrogen groups per molecule, alternatively at least three silicon bonded hydrogen groups per molecule selected from
- 10 one or more of
- C-1 a trimethyl or dimethyl hydrogen terminated polydimethyl methylhydrogen methylsilsesquioxane siloxane;
- C-2 a trimethyl or dimethyl hydrogen terminated polymethyl hydrogen siloxane;
- C-3 a dimethyl hydrogen terminated polydimethyl methylhydrogen siloxane;
- 15 C-4 an organosilicon resin;
- C-5 a cyclic siloxane;
- wherein the molar ratio of silicon bonded hydrogen groups to alkenyl groups and alkynyl groups in the composition is from 1:1 to 5:1;
- d) a hydrosilylation cure catalyst;
- 20 e) an organosilicon resin containing M and Q units and optionally Mvi units,
- f) an adhesion promoter comprising a mixture and/or reaction product of
- i) one or more alkoxy silanes having an epoxy group in the molecule;
- ii) a linear organopolysiloxane oligomer containing at least one alkenyl group and at least one hydroxy or alkoxy group per molecule; and
- 25 iii) an organometallic condensation reaction catalyst comprising organoaluminum or organozirconium compounds.
2. A composition in accordance with claim 1 wherein the molar ratio of silicon bonded hydrogen groups to alkenyl groups and alkynyl groups in the composition is from 1:1 to 5:1 in accordance with ASTM E168 and/or the cross-linker is present in an amount
- 30 of from 1 to 30 % weight.

3. A composition in accordance with any preceding claim wherein adhesion promoter (f) is typically present in the composition in a cumulative amount of (f)(i),(ii) and (iii) of from about 0.3 to 6% wt. of the composition.
4. A composition in accordance with any preceding claim wherein component (f) (i) is  
5 selected from 3-glycidoxypropyl trimethoxysilane, 3-glycidoxypropyl triethoxysilane, 3-glycidoxypropyl methyltrimethoxysilane, 4-glycidoxybutyl trimethoxysilane, 5,6-epoxyhexyl triethoxysilane, 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane, or 2-(3,4-epoxycyclohexyl) ethyltriethoxysilane and/or is present in an amount of from 0.1 to 5% by weight of the composition.
- 10 5. A composition in accordance with any preceding claim wherein component (f) (ii) is a methylvinylpolysiloxane in which both molecular terminals are dimethylhydroxysiloxy units, or a copolymer of a methylvinyl siloxane and dimethylsiloxane units in which both molecular terminals are dimethylhydroxysiloxy units, in each case having a viscosity not exceeding 500 mPa.s at 25° C and/or is present in an amount of from 0.1 to 5% by weight  
15 of the composition.
6. A composition in accordance with any preceding claim wherein component (f) (iii) is a zirconate based catalyst selected from zirconium tetrapropylate and zirconium tetrabutylate, tetra-isopropyl zirconate, zirconium (IV) tetraacetyl acetate, zirconium (IV) hexafluoroacetyl acetate, zirconium (IV) trifluoroacetyl acetate,  
20 tetrakis (ethyltrifluoroacetyl acetate) zirconium, tetrakis (2,2,6,6-tetramethyl-heptanethionate) zirconium, zirconium (IV) dibutoxy bis(ethylacetate), zirconium tributoxyacetylacetate, zirconium butoxyacetylacetate bisethylacetoacetate, zirconium butoxyacetylacetate bisethylacetoacetate, diisopropoxy bis (2,2,6,6-tetramethyl-heptanethionate) zirconium, or zirconium complexes having  $\beta$ -diketones.
- 25 7. A composition in accordance with any preceding claim wherein the composition additionally comprises an inhibitor to inhibit the cure of the composition.
8. A composition in accordance with any preceding claim wherein the composition is stored in two parts, Part A and Part B in which Part A comprises components a, b, d, f(iii) and optionally e and Part B comprises components a, b, c, f(i), f(ii) and optionally e.

9. A composition in accordance with any preceding claim which upon cure on a fabric substrate has a total volatile organic compound content of < 40ppm when tested in accordance with VDA277.
10. An airbag fabric coated with an elastomeric coating which is a cured product of the hydrosilylation curable textile coating composition in accordance with any preceding claim.
11. An airbag fabric coated with an elastomeric coating in accordance with claim 10 has a total volatile organic compound content of < 40ppm when tested in accordance with VDA277.
12. A method of coating a textile with a hydrosilylation curable textile coating composition in accordance with any one of claims 1 to 9 by mixing the composition together, coating a textile with the composition and curing the composition on the textile.
13. A method of coating a textile with a hydrosilylation curable textile coating composition in accordance with any one of claims 1 to 9 wherein the textile is coated by spraying, gravure coating, bar coating, coating by knife-over-roller, coating by knife-over-air, padding, dipping and screen-printing and/or is applied at a coat-weight of from 10 g/m<sup>2</sup> to 150 g/m<sup>2</sup>.
14. Use of a composition in accordance with any one of claims 1 to 9 to provide a coated textile with an improved TVOC.
15. Use in accordance with claim 14 wherein the coated textile has a total volatile organic compound content of < 40ppm when tested in accordance with VDA277.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2019/098274

**A. CLASSIFICATION OF SUBJECT MATTER**

C09D 183/05(2006.01)i; C09D 183/07(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)

C09D183

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)

CNPAT;CNKI;DWPI: airbag, textile, cloth, fabric, hydrosilylation, alkenyl, alkynyl, epoxy, methyl, hydrogen, linear, cyclic, hydroxy, alkoxy, aluminum, zirconium

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 102686686 A (DOW CORNING CORP) 19 September 2012 (2012-09-19) description, paragraphs [0009]-[0046]	1-15
X	US 2009001690 A1 (SHINETSU CHEM CO LTD) 01 January 2009 (2009-01-01) description, paragraphs [0005]-[0063]	1-15
X	CN 101163747 A (DOW CORNING CORP) 16 April 2008 (2008-04-16) description, paragraphs [0010]-[0049]	1-15
X	US 2011064882 A1 (SHINETSU CHEM CO LTD) 17 March 2011 (2011-03-17) description, paragraphs [0005]-[0076]	1-15
X	CN 102844379 A (DOW CORNING TORAY CO LTD et al.) 26 December 2012 (2012-12-26) description, paragraphs [0013]-[0078]	1-15
X	CN 103131327 A (SHINETSU CHEM IND CO LTD) 05 June 2013 (2013-06-05) description, paragraphs [0007]-[0131]	1-15
X	US 2007281564 A1 (SHINETSU CHEMICAL CO) 06 December 2007 (2007-12-06) description, paragraphs [0010]-[0065]	1-15

 Further documents are listed in the continuation of Box C. See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier 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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

03 April 2020

Date of mailing of the international search report

23 April 2020

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

MA,Zhenpeng

Facsimile No. (86-10)62019451

Telephone No. 86-(010)-62084940

**INTERNATIONAL SEARCH REPORT**  
**Information on patent family members**

International application No.

**PCT/CN2019/098274**

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	102686686	A	19 September 2012	JP	2013516520	A	13 May 2013
				WO	2011082134	A1	07 July 2011
				US	2012289110	A1	15 November 2012
				KR	20120110149	A	09 October 2012
				EP	2519595	A1	07 November 2012
				CA	2782143	A1	07 July 2011
US	2009001690	A1	01 January 2009	EP	2009059	A3	12 August 2009
				EP	2009059	B1	20 October 2010
				US	7641980	B2	05 January 2010
				DE	602008003060	D1	02 December 2010
				KR	20090004546	A	12 January 2009
				JP	2009007468	A	15 January 2009
				KR	101130604	B1	02 April 2012
				EP	2009059	A2	31 December 2008
CN	101163747	A	16 April 2008	GB	0302491	D0	05 March 2003
				CN	101163747	B	16 November 2011
US	2011064882	A1	17 March 2011	EP	2295512	A1	16 March 2011
				JP	2011080037	A	21 April 2011
				JP	5397350	B2	22 January 2014
				US	8608846	B2	17 December 2013
				EP	2295512	B1	21 March 2012
CN	102844379	A	26 December 2012	US	8962498	B2	24 February 2015
				CA	2791520	C	09 January 2018
				EP	2563861	A1	06 March 2013
				CA	2791520	A1	03 November 2011
				JP	2013531695	A	08 August 2013
				CN	102844379	B	25 February 2015
				US	2013071591	A1	21 March 2013
				EP	2563861	B8	25 July 2018
				KR	101768111	B1	14 August 2017
				WO	2011137121	A1	03 November 2011
				KR	20130069554	A	26 June 2013
				JP	5711357	B2	30 April 2015
				EP	2563861	B1	26 July 2017
				CN	103131327	A	05 June 2013
JP	2013087203	A	13 May 2013				
CN	103131327	B	15 June 2016				
US	2013099468	A1	25 April 2013				
US	8785586	B2	22 July 2014				
EP	2584004	B1	02 August 2017				
JP	5605345	B2	15 October 2014				
US	2007281564	A1	06 December 2007				
				US	7838118	B2	23 November 2010
				CA	2591146	A1	06 December 2007
				DE	602007000527	D1	26 March 2009
				EP	1865039	B1	11 February 2009