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(54) Title: SEALANT COMPOSITION

(57) Abstract: This relates to a one-part condensation curable silicone composition comprising a titanium-based reaction product obtained or obtainable from a process comprising the steps of (i) mixing a first ingredient, an alkoxy titanium compound having from 2 to 4 alkoxy groups with a second ingredient, a linear or branched polydiorganosiloxane polymer having at least two terminal silanol groups per molecule; (ii) enabling the first and second ingredients to react together by stirring under vacuum to form a reaction product; and collecting the reaction product of step (ii). It was identified that such a composition was suitable for use in humid climates i.e., hot and damp climates having high temperatures (e.g., greater than or equal to (≥) 30°C) and high relative humidity (RH) (e.g., greater than or equal to 75%RH) which is storage stable for at least 4 months.

SEALANT COMPOSITION

This relates to a one-part condensation curable silicone composition comprising a titanium-based reaction product obtained or obtainable from a process comprising the steps of (i) mixing a first ingredient, an alkoxy titanium compound having from 2 to 4 alkoxy groups with a second ingredient, a linear or branched polydiorganosiloxane polymer having at least two terminal silanol groups per molecule; (ii) enabling the first and second ingredients to react together by stirring under vacuum to form a reaction product; and collecting the reaction product of step (ii). It was identified that such a composition was suitable for use in humid climates i.e., hot and damp climates having high temperatures (e.g., greater than or equal to (≥) 30°C) and high relative humidity (RH) (e.g., greater than or equal to 75% RH) which is storage stable for at least 4 months.

It is well known to those skilled in the art that alkoxy titanium compounds, i.e., alkyl titanates, are suitable catalysts for one component moisture curable silicone compositions designed to be cured in temperate climates, e.g., from about 10 to 30°C, more usually from about 10 to 25°C. One-part condensation curing silicone compositions containing titanate catalysts have been widely described as skin or diffusion curing one-part condensation silicone elastomer compositions. Skin or diffusion cure (e.g., moisture/condensation) takes place by the formation of a cured skin at the composition/air interface subsequent to the sealant/encapsulant being applied on to and/or between one or more substrates. It involves the diffusion of moisture from the sealant/encapsulant interface with air to the inside (or core) of the layer of silicone composition applied, the diffusion of condensation reaction by-product/effluent from the inside (or core) to the outside (or surface) of the curing material and the gradual thickening of the cured skin over time from the outside/surface to the inside/core.

Given such one-part compositions are stored before use in a single composition they need to contain as little water/moisture as possible to prevent cure during the storage. Because the diffusion of moisture/water into the bulk of the curing composition is a lengthy process, such one-part sealant compositions are usually applied on or between the one or more substrates in a layer that is no thicker than about 15 mm. Layers thicker than 15 mm are known to lead to uncured material in the depth of the material due to the inability of the moisture from the air/sealant interface to penetrate far enough into the bulk of the sealant applied.

However, because of their sensitivity to water, such titanate catalysts are usually not suitable in hotter climates, particularly hot and humid climates, i.e., where the temperature is regularly above 30°C and the relative humidity of at least 75% because alkoxy-titanium bonds (titanate bonds) are sensitive to hydrolysis (e.g., the cleavage of bonds of functional groups by reaction with water). Titanate compounds can quickly hydrolyse, especially at elevated temperatures, liberating the corresponding alcohol with respect to the alkoxy group(s) bound to the titanium.

Hence, in the presence of moisture, tetra alkyl titanate catalysts can fully hydrolyse to form titanium (IV) hydroxide ($Ti(OH)_4$), which is of only limited solubility in silicone-based compositions. Crucially, the formation of titanium hydroxides such as titanium (IV) hydroxide dramatically decreases the catalytic efficiency of the titanium-based compound(s) provided as catalysts for curing condensation curable silicone compositions, leading to a very slow skin curing in hot and humid situations. In these conditions, the alkoxy titanium present at the sealant/air interface of the curing sealant will be fully hydrolysed, resulting in a highly tacky surface, while the bulk of the sealant may have cured properly as there is limited solubility of moisture in the product.

This issue is not seen with tin (IV) catalysts because they are not similarly affected by water. However tin cured condensation systems can undergo reversion (i.e., depolymerisation) at especially in confinement at temperatures above 80°C and in a humid environment. Moreover, formulations based on tin (IV) catalysts are difficult to stabilize for a long storage. Hence, titanium-based catalysts tend to be preferred over tin (IV) based catalysts in high temperature environments but they can't match the speed of cure of sealants cured with tin (IV) catalysts and this issue is exacerbated in humid climates because of their exposure to moisture.

In silicone compositions stored before use in two or more parts, a first part contains a filler which typically contains the moisture required to activate condensation cure in the bulk of the product. Unlike the previously mentioned diffusion cure one-part system, two-part condensation cure systems, once the two parts have been mixed together, cure simultaneously throughout the whole of sealant (often referred to as "bulk cure"). Such bulk cure two-part sealants are therefore known to generally cure quicker than one-part (diffusion cure) sealants and are better suited when thicker layers of sealant i.e., sections greater than 15 mm in depth are required.

If a skin is formed at the air/sealant interface, it will be only in the first minutes after application. Soon after, the product will become a solid throughout the entire mass.

Until recently, titanate catalysts i.e., tetra alkyl titanates (e.g. $Ti(OR)_4$ where R is an alkyl group having at least one carbon) and chelated titanates were not used in or as curing agents for curing two-part condensation curable compositions because of their sensitivity to hydrolysis in the presence of water (as discussed previously) or alcoholysis in the presence of alcohol, resulting in the general understanding the industry that such two-part condensation curable compositions require tin catalysts. However, contrary to historical expectations it was recently determined that in some instances titanium-based catalysts may be utilised in or as curing agents in multi-part, e.g., two-part, compositions designed for condensation "bulk cure" of silicone-based compositions (e.g., WO2018024858 and WO2019027668). This is helpful to many users because of the susceptibility of tin cured condensation systems to reversion (i.e., depolymerisation) at temperatures above 80°C and/or in humid conditions which is a major issue for high temperature where cured elastomers are going to be exposed to heat e.g., electronics applications. However, whilst this is a significant benefit, the titanium-based catalysts when used in or as curing agents in said two-part compositions

cannot match the speed of cure obtained with tin (IV) catalysts. This led to the development of the intermediate generated in WO2022/108893 and the two-part silicone sealant composition obtained in WO2022108896 containing said intermediate for accelerating cure speed in such two-part systems.

However, a need remains to overcome the long-term problem that one part-sealant compositions formulated using standard titanium catalysts are curing too slowly in hot and humid climates such as on the Indian and African continents due to the instability of the standard titanate catalysts when exposed to moisture.

There is provided herein a one-part condensation curable silicone composition comprising:

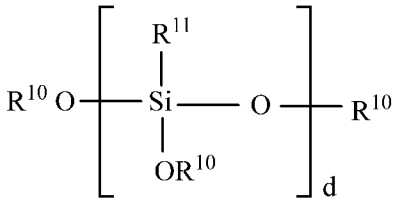
(a) an organopolysiloxane polymer of the formula

$X_{3-n}R_nSi\text{-}Z\text{-}(R^1_ySiO_{(4-y)/2})_z\text{–}SiR^1_2\text{-}Z\text{-}Si\text{-}R_nX_{3-n}$ (1)

in which each X is independently an alkoxy group, each R is an alkyl, alkenyl or aryl group, each R^1 is an X group, alkyl group, alkenyl group or aryl group and Z is oxygen or a divalent organic group;

n is 0 or 1, y is 0, 1 or 2, preferably 2 and z is an integer such that said organopolysiloxane polymer has a viscosity of from 10,000 to 150,000 mPa.s at 25°C, in an amount of from 30 to 80 weight % (wt. %) of the composition;

(b) a cross-linker of the structure:



Wherein each R^{10} may be the same or different and is an alkyl group having from 1 to 8 carbons, and each R^{11} is an alkenyl group having from 2 to 6 carbons and d is from 1 to 10;

(c) a titanium-based reaction product obtained or obtainable from a process comprising the steps of:

(i) mixing a first ingredient, an alkoxy titanium compound having from 2 to 4 alkoxy groups with a second ingredient, a linear or branched polydiorganosiloxane polymer having at least two terminal silanol groups per molecule;

(ii) enabling the first and second ingredients to react together by stirring under vacuum to form a reaction product; and

collecting the reaction product of step (ii); and

(d') a filler comprising one or more of precipitated calcium carbonate, ground calcium carbonate, precipitated silica, fumed silica or a mixture thereof which filler has been hydrophobically treated;

wherein the molar ratio of OH groups : alkoxy groups is in the range of from 0.09 : 1 to 0.1375 : 1.

Such a one-part condensation curable silicone composition is room temperature curable but advantageously the one-part condensation curable silicone composition is storage stable and curable at a temperature of at least 30° C and greater than relative humidity of 75 % measured using a

suitable hygrometer and may be utilised as a sealant and/or adhesive. There are a wide range of hygrometers which can be used, including for the sake of example an EXTECH humidity and temperature recorder, Model RH520 commercially available from the Extech Instrumentation Corporation, a Triplett RHT22 Temperature-Humidity Indicator, a Thermopro TP50 Hygrometer, a Thermopro TP55 Hygrometer, a Beurer HM16 Hygrometer, a Noklead Hygrometer, a TFA Dostmann Moxx Hygrometer or a TFA Dostmann Cosy Hygrometer or the like. Of the above, an EXTECH humidity and temperature recorder, Model RH520 commercially available from the Extech Instrumentation Corporation was preferred.

For the avoidance of doubt, relative humidity is the amount of water vapour present in air expressed as a percentage of the amount needed for saturation at the same temperature. It is generally determined using a suitable hygrometer such as those listed above. It is considered to indicates a present state of absolute humidity relative to the maximum humidity for the same temperature. A higher value of a higher percentage means that the air–water mixture is more humid. At 100% relative humidity, the air is saturated and is at its dew point. In the absence of a foreign body on which droplets or crystals can form the relative humidity can exceed 100%, in which case the air is said to be supersaturated.

Absolute humidity may be expressed as either:

(i) The mass of water vapor per volume of moist air (g/m^3) or as

(ii) The mass of water vapor per mass of dry air (g/kg).

There is also provided a method for preparing a one-part condensation curable silicone composition comprising the steps of:

Preparing a titanium-based reaction product (c) with a process comprising the steps of:

(i) mixing a first ingredient, an alkoxy titanium compound having from 2 to 4 alkoxy groups with a second ingredient, a linear or branched polydiorganosiloxane polymer having at least two terminal silanol groups per molecule;

(ii) enabling the first and second ingredients to react together by stirring under vacuum to form a reaction product; and

collecting the reaction product of step (ii); and mixing said titanium-based reaction product (c) with the other components of the one-part silicone composition, namely:

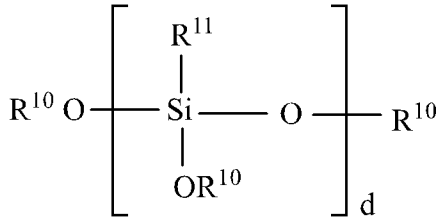
(a) an organopolysiloxane polymer of the formula

$X_{3-n}R_nSi\text{-}Z\text{-}(R^1_ySiO_{(4-y)/2})_z\text{–}SiR^1_2\text{-}Z\text{-}Si\text{-}R_nX_{3-n}$ (1)

in which each X is independently an alkoxy group, each R is an alkyl, alkenyl or aryl group, each R^1 is an X group, alkyl group, alkenyl group or aryl group and Z is oxygen or a divalent organic group;

n is 0 or 1, y is 0, 1 or 2, preferably 2 and z is an integer such that said organopolysiloxane polymer has a viscosity of from 10,000 to 150,000 mPa.s at 25°C, in an amount of from 30 to 80 weight % (wt. %) of the composition;

(b) a cross-linker of the structure:



Wherein each R^{10} may be the same or different and is an alkyl group having from 1 to 8 carbons, and each R^{11} is an alkenyl group having from 2 to 6 carbons and d is from 1 to 10;

and

(d') a filler comprising one or more of precipitated calcium carbonate, ground calcium carbonate, precipitated silica, fumed silica or a mixture thereof which filler has been hydrophobically treated;

wherein the molar ratio of OH groups : alkoxy groups is in the range of from 0.09 : 1 to 0.1375 : 1.

Such a one-part condensation curable silicone composition is room temperature curable but advantageously the one-part condensation curable silicone composition made in accordance with the above process is storage stable and curable at a temperature of at least 30° C and greater than relative humidity of 75 % determined using a hygrometer and may be utilised as a sealant and/or adhesive. There are a wide range of hygrometers which can be used, including for the sake of example an EXTECH humidity and temperature recorder, Model RH520 commercially available from the Extech Instrumentation Corporation, a Triplett RHT22 Temperature-Humidity Indicator, a Thermopro TP50 Hygrometer, a Thermopro TP55 Hygrometer, a Beurer HM16 Hygrometer, a Noklead Hygrometer, a TFA Dostmann Moxx Hygrometer or a TFA Dostmann Cosy Hygrometer or the like. Of the above, an EXTECH humidity and temperature recorder, Model RH520 commercially available from the Extech Instrumentation Corporation was preferred.

There is also provided a silicone material which is the cured product of the one-part condensation curable silicone composition described above and or the one-part condensation curable silicone composition made by the method described above.

There is also provided a use of one-part condensation curable silicone composition comprising:

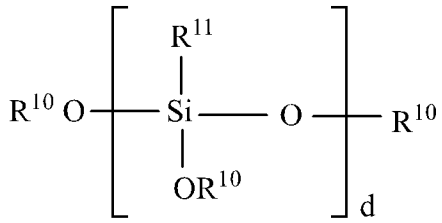
(a) an organopolysiloxane polymer of the formula

$$X_{3-n}R_nSi\text{-}Z\text{-}(R'_ySiO_{(4-y)/2})_z\text{–}SiR'_2\text{-}Z\text{-}Si\text{-}R_nX_{3-n} \qquad (1)$$

in which each X is independently an alkoxy group, each R is an alkyl, alkenyl or aryl group, each R^1 is an X group, alkyl group, alkenyl group or aryl group and Z is oxygen or a divalent organic group;

n is 0 or 1, y is 0, 1 or 2, preferably 2 and z is an integer such that said organopolysiloxane polymer has a viscosity of from 10,000 to 150,000 mPa.s at 25°C, in an amount of from 30 to 80 weight % (wt. %) of the composition;

(b) a cross-linker of the structure:



Wherein each R^{10} may be the same or different and is an alkyl group having from 1 to 8 carbons, and each R^{11} is an alkenyl group having from 2 to 6 carbons and d is from 1 to 10;

(c) a titanium-based reaction product obtained or obtainable from a process comprising the steps of:

(i) mixing a first ingredient, an alkoxy titanium compound having from 2 to 4 alkoxy groups with a second ingredient, a linear or branched polydiorganosiloxane polymer having at least two terminal silanol groups per molecule;

(ii) enabling the first and second ingredients to react together by stirring under vacuum to form a reaction product; and

collecting the reaction product of step (ii); and

(d') a filler comprising one or more of precipitated calcium carbonate, ground calcium carbonate, precipitated silica, fumed silica or a mixture thereof which filler has been hydrophobically treated;

wherein the molar ratio of OH groups : alkoxy groups is in the range of from 0.09 : 1 to 0.1375 : 1;

as a one-part condensation curable silicone composition curable at a temperature of at least 30°C and greater than relative humidity of 75 % determined using a hygrometer.

There are a wide range of hygrometers which can be used, including for the sake of example an EXTECH humidity and temperature recorder, Model RH520 commercially available from the Extech Instrumentation Corporation, a Triplett RHT22 Temperature-Humidity Indicator, a Thermopro TP50 Hygrometer, a Thermopro TP55 Hygrometer, a Beurer HM16 Hygrometer, a Noklead Hygrometer, a TFA Dostmann Moxx Hygrometer or a TFA Dostmann Cosy Hygrometer or the like. Of the above, an EXTECH humidity and temperature recorder, Model RH520 commercially available from the Extech Instrumentation Corporation was preferred.

Use of a titanium-based reaction product (c) obtained or obtainable from a process comprising the steps of:

(i) mixing a first ingredient, an alkoxy titanium compound having from 2 to 4 alkoxy groups with a second ingredient, a linear or branched polydiorganosiloxane polymer having at least two terminal silanol groups per molecule;

(ii) enabling the first and second ingredients to react together by stirring under vacuum to form a reaction product; and

collecting the reaction product of step (ii);

in a one-part condensation curable silicone composition otherwise comprising:

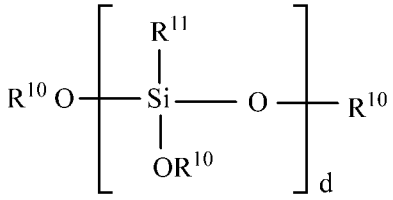
(a) an organopolysiloxane polymer of the formula

$$X_{3-n}R_nSi\text{-}Z\text{-}(R^1{}_ySiO_{(4-y)/2})_z\text{–}SiR^1{}_2\text{-}Z\text{-}Si\text{-}R_nX_{3-n} \quad (1)$$

in which each X is independently an alkoxy group, each R is an alkyl, alkenyl or aryl group, each R^1 is an X group, alkyl group, alkenyl group or aryl group and Z is oxygen or a divalent organic group;

n is 0 or 1, y is 0, 1 or 2, preferably 2 and z is an integer such that said organopolysiloxane polymer has a viscosity of from 10,000 to 150,000 mPa.s at 25°C, in an amount of from 30 to 80 weight % (wt. %) of the composition;

(b) a cross-linker of the structure:



Wherein each R^{10} may be the same or different and is an alkyl group having from 1 to 8 carbons, and each R^{11} is an alkenyl group having from 2 to 6 carbons and d is from 1 to 10;

and

(d') a filler comprising one or more of precipitated calcium carbonate, ground calcium carbonate, precipitated silica, fumed silica or a mixture thereof which filler has been hydrophobically treated;

wherein the molar ratio of OH groups : alkoxy groups is in the range of from 0.09 : 1 to 0.1375 : 1;

in or for a one-part silicone composition curable at a temperature of at least 30°C and greater than relative humidity of 75 % determined using a hygrometer.

There are a wide range of hygrometers which can be used, including for the sake of example an EXTECH humidity and temperature recorder, Model RH520 commercially available from the Extech Instrumentation Corporation, a Triplett RHT22 Temperature-Humidity Indicator, a Thermopro TP50 Hygrometer, a Thermopro TP55 Hygrometer, a Beurer HM16 Hygrometer, a Noklead Hygrometer, a TFA Dostmann Moxx Hygrometer or a TFA Dostmann Cosy Hygrometer or the like. Of the above, an EXTECH humidity and temperature recorder, Model RH520 commercially available from the Extech Instrumentation Corporation was preferred.

The components of the composition will now be described in more detail.

Organopolysiloxane polymer having at least two hydrolysable groups per molecule (a)

The organopolysiloxane polymer having at least two hydrolysable groups per molecule (a) described above is of the formula:

$$X_{3-n}R_nSi\text{-}Z\text{-}(R^1_ySiO_{(4-y)/2})_z\text{–}SiR^1_2\text{-}Z\text{-}Si\text{-}R_nX_{3-n} \qquad (1)$$

in which each X is independently a hydrolysable group, each R is an alkyl, alkenyl or aryl group, each R^1 is an X group or an R group and Z is oxygen or a divalent organic group;

n is 0, 1, 2 or 3; y is 0, 1 or 2, preferably 2 and z is an integer such that said organopolysiloxane polymer has a viscosity of from 10,000 to 150,000 mPa.s at 25°C. The organopolysiloxane polymer (a) described above is present in the composition in an amount of from 30 to 90 weight % (wt. %) of the composition.

In the above formula each X is independently a hydrolysable group, alternatively an alkoxy group having from 1 and 10 carbons. Illustrative alkoxy groups are methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, t-butoxy, isobutoxy, pentoxy, hexoxy and 2-ethylhexoxy; dialkoxy groups, such as methoxymethoxy or ethoxymethoxy an alkoxyaryloxy, such as ethoxyphenoxy groups; alternatively, each X is an alkoxy group having from one and six carbons, alternatively having from one and four carbons or alternatively is a methoxy or ethoxy group.

Each R group is an alkyl, alkenyl or aryl group, alternatively each R is an alkyl group having from 1 to 6 carbons, an alkenyl group having from 2 to 6 carbons such as vinyl, allyl and hexenyl groups or an aryl group having from 6 to 12 carbons; alternatively, each R is an alkyl group having from 1 to 6 carbons, or an aryl group having from 6 to 12 carbons; alternatively each R is an alkyl group having from 1 to 6 carbons, alternatively each R is an ethyl group or a methyl group. In one embodiment R may include substituted aliphatic organic groups such as 3,3,3-trifluoropropyl groups aminoalkyl groups, polyaminoalkyl groups, and/or epoxyalkyl groups.

Each R^1 is an X group, or an R group, with the proviso that cumulatively at least two X groups and/or R^1 groups per molecule are hydrolysable groups, alternatively an alkoxy group. Alternatively, each R^1 is an R group. It is possible that some R^1 groups may be siloxane branches off the polymer backbone which branches may have terminal groups as hereinbefore described.

Each Z may be the same of different and is oxygen or a divalent organic group. When Z is a divalent organic group, it is typically an alkylene having from 2 to 10 carbons, such as for example, an ethylene, propylene, butylene, pentylene and/or hexylene group; alternatively, an alkylene group having 2 to 6 carbons, alternatively an alkylene group having from 2 to 5 carbons. Subscript n is zero 1, 2 or 3 but may only be 3 or 2 when R^1 contains the required minimum number of hydrolysable groups. In one embodiment n is 0, 1 or 2, in a further alternative n is 0 or 1 in which case no R^1s will be required to contain a hydrolysable group or alkoxy group. alternatively, is zero; each subscript y is 0, 1 or 2, and is preferably 2. In one embodiment each n is zero and each Z is an alkylene having from 2 to 10 carbons.

Whilst y is 0, 1 or 2, substantially y= 2, e.g., at least 90%, alternatively 95% of $R^1_ySiO_{(4-y)/2}$ groups are characterized with y = 2. Subscript z is an integer such that said organopolysiloxane polymer has a viscosity of from 10,000 to 150,000 mPa.s, alternatively from 30,000 to 140,000mPa.s at 25°C, therefore z is an integer of from approximately 300 to 2000. The viscosity of component (a) may be measured at 25°C in accordance with the ASTM D4287 Cone and Plate Method using a Brookfield DV-III Ultra Rheometer.

Component (a) is present in the one-part condensation curable silicone composition in an amount of from 30 to 90 wt. % of the composition, alternatively 30 to 80 wt. % of the composition alternatively 35 to 75 wt. % of the composition, alternatively 35 to 60 wt. % of the composition.

Organopolysiloxane polymer (a) can be a single siloxane represented by Formula (1) or it can be mixtures of organopolysiloxane polymers represented by the aforesaid formula. Hence, it may be a

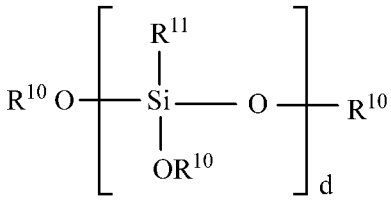
"siloxane polymer mixture" so organopolysiloxane polymer (a) is meant to include any individual organopolysiloxane polymer (a) or mixtures of organopolysiloxane polymer (a).

The Degree of Polymerization (DP), (i.e., in the above formula substantially z), is usually defined as the number of monomeric units in a macromolecule or polymer or oligomer molecule of silicone. Synthetic polymers 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 (Mn) and the weight average molecular weight (Mw). The Mn and Mw of a silicone polymer can be determined by gel permeation chromatography (GPC) with precision of about 10-15% using polystyrene standards.

This technique is standard and yields Mw, Mn and polydispersity index (PI). The degree of polymerisation (DP) =Mn/Mu where Mn is the number-average molecular weight coming from the GPC measurement and Mu is the molecular weight of a monomer unit. PI=Mw/Mn. The DP is linked to the viscosity of the polymer via Mw, the higher the DP, the higher the viscosity. In the present disclosure the number average molecular weight and weight average molecular weight values of component (a) herein may, for example, be determined using a Waters 2695 Separations Module equipped with a vacuum degasser, and a Waters 2414 refractive index detector (Waters Corporation of MA, USA). The analyses may then be performed using certified grade toluene flowing at 1.0 mL/min as the eluent. Data collection and analyses may be performed using Waters Empower GPC software.

Component (b) Cross-Linker

Component (b) is a cross-linker of the structure:



Wherein each R^{10} may be the same or different and is an alkyl group having from 1 to 8 carbons, and each R^{11} is an alkenyl group having from 2 to 8 carbons and d is from 1 to 10. Preferably component (b) is a trialkoxyalkenyl silane having one silicon said but it may also be an oligomer of said trialkoxyalkenyl silane containing from 2 to 10 silicons.

Each R^{10} may be the same or different and is an alkyl group having from 1 to 8 carbons. In one alternative may be linear or branched and may be a methyl group, and ethyl group, a propyl group, an isopropyl group an n-butyl group, a tertiary-butyl group, an isobutyl group, a pentyl group a hexyl group or a 2-ethylhexyl group, alternatively R^{10} may be the same or different and is an alkyl group having from 1 to 3 carbons such as a methyl, ethyl isopropyl or propyl group.

R^{11} is an alkenyl group having from 2 to 8 carbons such as a vinyl group, a propenyl group, an isopropenyl group an n-butenyl group, a pentenyl group a hexenyl group or a 2-ethylhexenyl group or suitable branched isomers thereof.

In one embodiment cross-linker (b) comprises at least one of trimethoxyvinyl silane, triethoxyvinyl silane or an oligomer thereof. Subscript d' is from 1 to 10, alternatively 1 to 8, alternatively 1 to 6, alternatively 1 to 4.

Component (b) is present in a range of from 1 to 10 wt. % of the one-part condensation curable silicone composition, alternatively from 1.25 to 7.5 weight % of the composition, alternatively from 1.5 to 5.0 weight % of the composition.

As previously identified the molar ratio of OH groups : alkoxy groups is in the range of from 0.09 : 1 to 0.1375 : 1.

The molar amount of the alkoxy groups present e.g., methoxy groups present is substantially, if not totally the alkoxy content from polymer (a) and the alkoxy content of component (b) the cross-linker and was calculated as follows:

Total alkoxy content (Molar) = molar alkoxy from component (a) + molar alkoxy from component (b) which are calculated as follows:

Molar alkoxy content of polymer (a) = (wt. of polymer/ wMW) x no of alkoxy groups present

So, for a polymer with a weight average molecular weight of 116,500 wherein n from formula 1 above is zero and there are 6 alkoxy groups per molecule,

Molar alkoxy content of polymer (a) = (wt. of polymer/ 116,500) x 6

and

Molar alkoxy content of cross-linker (b)

= (the weight of the cross-linker added/MW of the cross-linker) x No of alkoxy groups

So, in the case of vinyl trimethoxysilane which has a molecular weight of 148.23 and three methoxy groups:

Molar alkoxy content of cross-linker (b) = (the weight of the cross-linker added/148.23) x 3.

It is to be understood that the value of d was known before the calculations were made and as such the value of d was accommodated into the above calculation as it was known if the cross-linker (b) used was e.g., a dimer, trimer, tetramer or pentamer. Furthermore, it was identified that all alkoxy groups had been stripped out of component (c) during its preparation and as such there was no contribution to the alkoxy calculation from component (c).

Component (c) the titanium-based reaction product

Component (c) of the composition is a titanium-based reaction product as described above, obtained or obtainable from a process comprising the steps of:

(i) mixing a first ingredient, an alkoxy titanium compound having from 2 to 4 alkoxy groups with a second ingredient, a linear or branched polydiorganosiloxane polymer having at least two terminal silanol groups per molecule;

(ii) enabling the first and second ingredients to react together by stirring under vacuum to form a reaction product; and

collecting the reaction product of step (ii).

Component (c), the titanium-based reaction product of the composition herein, is prepared by the reaction of a first and second ingredient. The first ingredient of the process to prepare component (c) is an alkoxy titanium compound having from 2 to 4 alkoxy groups, e.g., $Ti(OR^5)_4$, $Ti(OR^5)_3R^6$, $Ti(OR^5)_2R^6_2$ or a chelated alkoxy titanium molecule where there are two alkoxy (OR^5) groups present and a chelate bound twice to the titanium atom; where R^5 is a linear or branched alkyl group having from 1 to 20 carbons, alternatively 1 to 15 carbons, alternatively 1 to 10 carbons, alternatively 1 to 6 carbons and when present R^6 is an organic group such as an alkyl group having from 1 to 10 carbon atoms, an alkenyl group having from 2 to 10 carbon atoms, an alkynyl group having from 2 to 10 carbon atoms, a cycloalkyl group having from 3 to 10 carbon atoms, or a phenyl group having from 6 to 20 carbon atoms or a mixture thereof.

Each R^6 may optionally contain substituted groups with e.g., one or more halogen group such as chlorine or fluorine. Examples of R^6 may include but are not restricted to methyl, ethyl, propyl, butyl, vinyl, cyclohexyl, phenyl, tolyl group, a propyl group substituted with chlorine or fluorine such as 3,3,3-trifluoropropyl, chlorophenyl, beta-(perfluorobutyl)ethyl or chlorocyclohexyl group. However, typically each R^6 may be the same or different and is selected from an alkyl group, an alkenyl group or an alkynyl group, alternatively an alkyl group, an alkenyl group, alternatively an alkyl group, in each case having up to 10 carbons, alternatively, up to 6 carbons per group.

As mentioned above R^5 is a linear or branched alkyl group having from 1 to 20 carbons, include but are not restricted to methyl, ethyl, n-propyl, isopropyl, n-butyl, tertiary butyl and branched secondary alkyl groups such as 2, 4-dimethyl-3-pentyl. Suitable examples of the first ingredient when $Ti(OR^5)_4$, include for the sake of example, tetra methyl titanate, tetra ethyl titanate, tetra n-propyl titanate, tetra n-butyl titanate, tetra t-butyl titanate, tetraisopropyl titanate. When the first ingredient is $Ti(OR^5)_3\ R^6$, R^6 is typically an alkyl group and examples include but are not limited to trimethoxy alkyl titanium, triethoxy alkyl titanium, tri n-propoxy alkyl titanium, tri n-butoxy alkyl titanium, tri t-butoxy alkyl titanium and tri isopropoxy alkyl titanate.

The first ingredient, used to prepare component (c) of the composition herein, i.e., the alkoxy titanium compound having from 2 to 4 alkoxy groups, maybe present in an amount of from 0.01 wt. % to 20 wt. % of the total weight of the First ingredient + second ingredient.

The second ingredient used to prepare component (c) of the composition herein is a linear or branched polydiorganosiloxane having at least two terminal silanol groups per molecule. The second ingredient used to prepare component (c) of the composition herein may comprise an oligomer or polymer comprising multiple siloxane units of formula (2)

$$-(R^7_sSiO_{(4-s)/2})- \quad (2)$$

in which each R^7 is independently an organic group such as a hydrocarbyl group having from 1 to 10 carbon atoms optionally substituted with one or more halogen group such as chlorine or fluorine and s is 0, 1 or 2. In one alternative s is 2 and the linear or branched polydiorganosiloxane backbone is therefore linear although a small proportion of groups where s is 1 may be utilised to enable branching. For example, R^7 may include alkyl groups such as methyl, ethyl, propyl, butyl, alkenyl groups such as vinyl, propenyl, butenyl, pentenyl and or hexenyl groups, cycloalkyl groups such as cyclohexyl, and aromatic groups such as phenyl, tolyl group. In one alternative, R^7 may comprise alkyl groups, alkenyl groups and/or phenyl groups such as methyl, ethyl, propyl, butyl, alkenyl groups such as vinyl, propenyl, butenyl, pentenyl and or hexenyl groups, cycloalkyl groups such as cyclohexyl, and aromatic groups such as phenyl, tolyl group. Preferably, the polydiorganosiloxane chain is a polydialkylsiloxane chain, a polyalkylalkenylsiloxane chain or a polyalkylphenylsiloxane chain but co-polymers of any two or more of these may also be useful. When the second ingredient contains a polydialkylsiloxane chain, a polyalkylalkenylsiloxane chain and/or a polyalkylphenylsiloxane chain the alkyl groups usually comprises between 1 and 6 carbons; alternatively the alkyl groups are methyl and/or ethyl groups, alternatively the alkyl groups are methyl groups; the alkenyl groups usually comprises between 2 and 6 carbons; alternatively the alkenyl groups may be vinyl, propenyl, butenyl, pentenyl and or hexenyl groups, alternatively vinyl, propenyl, and/or hexenyl groups. In one alternative the polydiorganosiloxane is a polydimethylsiloxane chain, a polymethylvinylsiloxane chain or a polymethylphenylsiloxane chain, or a copolymer of two or all of these.

For the avoidance of doubt a polydiorganosiloxane polymer means a substance composed of a molecule of high molecular weight (generally having a number average molecular weight of greater than or equal to 10,000g/mol comprising a large number of $-(R^7_sSiO_{(4-s)/2})-$ units which show polymer-like properties and the addition or removal of one or a few of the units has a negligible effect on the properties. In contrast a polydiorganosiloxane oligomer is a compound with a regular repeating structure $-(R^7_sSiO_{(4-s)/2})-$ units having too low an average molecular weight e.g., a molecule consisting of a few monomer units, e.g., dimers, trimers, and tetramers are, for example, oligomers respectively composed of two, three, and four monomers.

When linear, each terminal group must contain one silanol group. For example, the polydiorganosiloxane maybe dialkylsilanol terminated, alkyl disilanol terminated or trisilanol terminated but is preferably dialkylsilanol terminated. When branched the second ingredient must have at least two terminal silanol (Si-OH) bonds per molecule and as such comprise at least two terminal groups which are dialkylsilanol groups, alkyl disilanol groups and/or trisilanol groups, but typically dialkylsilanol groups.

Typically, the second ingredient used to prepare component (c) of the composition herein, the titanium-based reaction product, will have a viscosity in the order of 30 to 300 000 mPa.s, alternatively 50 to 100 000 mPa.s at 25°C, alternatively 70 to 75,000 mPa.s at 25°C, alternatively 70

to 50,000 mPa.s at 25°C, alternatively 70 to 20,000 mPa.s at 25°C, alternatively 70 to 10,000 mPa.s at 25°C. The viscosity may be measured using any suitable means e.g., a Modular Compact Rheometer (MCR) 302 Anton Paar GmbH of Graz, Austria using the most suitable settings and plates for the viscosity concerned, for example using a 25mm diameter rotational plate with a gap of 0.3 mm at a shear rate of $1s^{-1}$.

The number average molecular weight (Mn) and weight average molecular weight (Mw) of silicone can also be determined by Gel permeation chromatography (GPC) using polystyrene calibration standards. This technique is a standard technique, and yields values for Mw (weight average), Mn (number average) and polydispersity index (PI) (where PI=Mw/Mn).

Mn values provided in this application have been determined by GPC and represent a typical value of the polydiorganosiloxane used. If not provided by GPC, the Mn may also be obtained from calculation based on the dynamic viscosity of said polydiorganosiloxane.

The reaction used to prepare component (c) the titanium-based reaction product of the composition herein, may be undertaken at any suitable temperature but typically commences at room temperature. The temperature may elevate during the reaction and/or stirring and if desired the ingredients may be heated during the reaction.

The reaction used to prepare component (c) of the composition herein takes place under vacuum with a view to removing at least 50 wt. %, alternatively at least 75 wt. % alternatively at least 90% of the total amount of alcoholic by-products generated during the reaction. The above may be determined via several analytical techniques of which the simplest is the determination of weight loss from the reaction product.

Without being tied to current understanding, it is believed that the main reaction products of the above reaction, when the first ingredient is $Ti(OR^5)_4$, is a mixture of

$$(R^5O)_nTi((OSi\ R^7_2)_m\text{-}OH)_{4-n} \qquad (3)$$

Where n is 0, 1 or 2, alternatively 0 or 1, but preferably the major product is where n is 0, i.e.,

$$Ti((OSi\ R^7_2)_m\text{-}OH)_4 \qquad (4)$$

Where m is the degree of polymerisation of the second ingredient and is an integer indicative (commensurate) of the viscosity thereof.

Similarly, when the first ingredient is substantially $Ti(OR^5)_3\ R^6$ it is believed that the main reaction products of the above reaction when a is 0 or 1, is

$$R^6\ (R^5O)_aTi((OSiR^7_2)_m\text{-}OH)_{3-a} \qquad (5)$$

but preferably the major product is where a is 0, i.e.,

$$R^6Ti((OSi\ R^7_2)_m\text{-}OH)_3 \qquad (6)$$

Where m is the degree of polymerisation of the second ingredient and is an integer indicative (commensurate) of the viscosity of the second ingredient.

Optionally, there may be a third ingredient used in the preparation of component (c) the titanium-based reaction product of the composition herein. When present, the third ingredient is a linear or

branched polydiorganosiloxane and may be an oligomer or polymer as described for the second ingredient. However, the third ingredient only has one terminal silanol group per molecule for use in the reaction described above to form a Si-O-Ti bond with the first ingredient. The other terminal group(s) of the third ingredient contain no silanol groups. The terminal groups containing no silanol groups may comprise R^7 groups as defined above, alternatively a mixture of alkyl and alkenyl R^7 groups, alternatively alkyl R^7 groups. Examples include trialkyl termination e.g., trimethyl or triethyl termination or dialkylalkenyl termination, e.g., dimethylvinyl or diethyl vinyl or methylethylvinyl termination or the like.

Typically the third ingredient used in the preparation of component (c) the titanium-based reaction product of the composition herein will also have a viscosity analogous to that of the second ingredient, in the order of 30 to 300 000 mPa.s, alternatively 50 to 100 000 mPa.s at 25°C, alternatively 70 to 75,000 mPa.s at 25°C, alternatively 70 to 50,000 mPa.s at 25°C, alternatively 70 to 20,000 mPa.s at 25°C, alternatively 70 to 10,000 mPa.s at 25°C. The viscosity may be measured using any suitable means e.g., a Modular Compact Rheometer (MCR) 302 Anton Paar GmbH of Graz, Austria using the most suitable settings and plates for the viscosity concerned, for example using a 25mm diameter rotational plate with a gap of 0.3 mm at a shear rate of $1s^{-1}$.

The third ingredient may be present in an amount of up to 75 wt. % of the combination of the weight of the first, second and third ingredients, whereby the third ingredient replaces the equivalent proportion of the second ingredient. However, preferably the third ingredient when present is present in an amount of no more than 50%, alternatively no more than 25% of the first, second and third ingredients. When the third ingredient is present one or more silanol groups in structures (3), (4), (5) or (6) may be replaced by an R^7 group, alternatively an alkyl group or an alkenyl group, alternatively an alkyl group. For example, in the case of structure (2) the reaction product may be that shown below in structure (2a):

$$(R^5O)_nTi\ ((OSi\ R^7_2)_m\text{-}\ R^7)_p((OSi\ R^7_2)_m\text{-}OH)_{4-n-p} \qquad (3a)$$

Where n is 0, 1 or 2, alternatively 0 or 1, p is 0, 1 or 2, alternatively 0 or 1, and n +p is less than or equal to 4 and m is as previously defined.

It is preferred not to include the third ingredient as a reactant in the preparation of component (c) the titanium-based reaction product of the composition herein as when catalysts of the type depicted in structures (3), (4), (5) or (6) are present the terminal silanol groups are potentially available for participation in the formation of the cured silicone network, which makes them useful in the fully formulated elastomers. This is clearly less likely to be the case when greater amounts of the third ingredient are used as a starting ingredient in the process to make the titanium-based reaction product which can be used as component (c) in the compositions described herein. However, the presence of some of the third ingredient in the starting materials may be useful to assist in obtaining the required modulus of elastomers cured using the product of the process described herein.

When the starting ingredients in the process used for the preparation of component (c) of the composition herein are the first and second ingredients, the molar ratio of silanol groups : titanium may be any suitable ratio equal to or greater than 2 : 1. However, it is preferred for the ratio to be within the range of from 5 : 1 to 15 : 1 alternatively from 7 : 1 to 15 : 1, alternatively from at least 8 : 1 to 11 : 1. Lower ratios seem to lead to the presence of more viscous reaction product and less first ingredient present resulting in slower gelling times.

The total silanol molar content is calculated for 100 g of first and second ingredients. The silanol molar content related to the second ingredient is equal to the amount in grams (g) of silanol containing polymer in 100g of the first and second ingredients divided by the number average molecular weight of the second ingredient multiplied by the average number of silanol functions present in the second ingredient, typically 2. If there are several silanol functional linear or branched polydiorganosiloxanes in the starting ingredients, the sum of the molar content of each polymer is determined and then the cumulative total from all the linear or branched polydiorganosiloxanesis added together to constitute the total silanol molar content in the formulation.

The molar amount of any starting ingredient was determined using the following calculation:

$$\frac{[\text{Weight in parts of the ingredient} \times 100]}{[\text{sum of all parts of the starting ingredients} \times \text{MW of the ingredient}]}$$

Hence, merely for example, when ingredient 1 is tetra n-butyl titanate (TnBT), if ingredient 1 and ingredient 2 were mixed in a weight ratio of 10:1, i.e., 10 parts of ingredient 2 to every one part by weight of ingredient 1, given the molecular weight of TnBT is 340; the calculation would be.

$$\frac{[\text{Weight in parts of TnBT (1)} \times 100]}{[\text{sum of all parts of the starting ingredients (11)} \times 340]}$$

$$= 0.0267 \text{ mole of catalyst per 100g of the composition.}$$

The -OH content utilised in the molar ratio of OH groups : alkoxy groups was calculated on the basis of two contributors:

1) The first was calculated based on the silanol content of component (c), assuming 1mol of titanium present corresponded to 4 moles of Si-OH;

The mole ratio of SiOH : Ti in preparing the Titanium-based reaction product is around 9.7 : 1. So the remaining Silanol content in the component (c) is equals to

$$[7.5 * \text{Ti mole ratio} - 4 * \text{Ti mole ratio}].$$

The Ti content in component (c) 1 is 0.01407mmol/g. The Ti mole content can be easily calculated based on the loading level of component (c) in the formulation.

The second was determined from the moisture content of filler. The moisture content in filler was determined using a Mettler Halogen Moisture Analyzer Model HR83 by determining the weight of the filler powder before and after being heated at 105°C for 20 minutes and the wt. % of water present was determined from the difference.

In one embodiment of the process used in the preparation of component (c) the titanium-based reaction product of the composition herein, the first ingredient is added to the second ingredient, or when the third ingredient is present, the first ingredient is added to a mixture of the second and third ingredients.

In an alternative embodiment used in the preparation of component (c) of the composition herein, the second ingredient may be introduced into the first ingredient. This embodiment is less convenient than the above because titanates of the type used as the first ingredient, from which volatile alcohols R^5-OH) are generated in accordance with chemical reactions (6) below, are generally flammable due to the moisture from environment because it will substantially always contain some alcohol residues. The flash point of the titanium catalyst depends on the alcohol flammability.

$Ti\text{-}OR^5 + H_2O$ (moisture from the air) -> $Ti\text{-}OH + R^5\text{-}OH$

$Ti\text{-}OR^5 + Si\text{-}OH$ -> $Ti\text{-}O\text{-}Si + R^5\text{-}OH$ (7)

Hence, this method will require an explosion proof manufacturing process and the second ingredient is introduced into the first ingredient in a gradual measured manner. This route is likely to lead, at least initially, to a more concentrated catalyst until gradually the content of the second ingredient is increased. This embodiment is also less favoured because it is more difficult to remove the alcoholic by-products as successfully and the content of the second ingredient is generally much larger than the first ingredient in weight and volume.

It was found however that there was no need for complicated separation techniques to be used to isolate specific titanium species as component (c) of the composition as the reaction product works very well without separation.

Component (d') filler

Component (d') is a filler comprising one or more of precipitated calcium carbonate, ground calcium carbonate, precipitated silica, fumed silica or a mixture thereof which filler has been hydrophobically treated. Preferably said fillers (d') are provided in a finely divided form. Typically, the surface area of the reinforcing filler (d') is at least 15 m^2/g in the case of ground and/or precipitated calcium carbonate measured in accordance with the BET method (ISO 9277: 2010), alternatively 15 to 50 m^2/g, alternatively 15 to 25 m^2/g.

Silica fillers have a typical surface area of at least 50 m^2/g in accordance with the BET method (ISO 9277: 2010). In the case of high surface area fumed silica and/or high surface area precipitated silica, these may have surface areas of from 75 to 400 m^2/g measured in accordance with the BET method (ISO 9277: 2010), alternatively of from 100 to 300 m^2/g in accordance with the BET method (ISO 9277: 2010).

The reinforcing fillers (d') are preferably hydrophobically treated for example with one or more aliphatic acids, e.g., a fatty acid such as stearic acid or a fatty acid ester such as a stearate, or with organosilanes, organosiloxanes, or organosilazanes hexaalkyl disilazane or short chain siloxane

diols to render the filler(s) hydrophobic and therefore easier to handle and obtain a homogeneous mixture with the other adhesive components. Specific examples organosilanes, organosiloxanes, or organosilazanes may include, but are not restricted to, silanol terminated trifluoropropylmethylsiloxane, silanol terminated vinyl methyl (ViMe) siloxane, silanol terminated methyl phenyl (MePh) siloxane, liquid hydroxyldimethyl-terminated polydiorganosiloxane containing an average from 2 to 20 repeating units of diorganosiloxane in each molecule, hydroxyldimethyl terminated phenylmethyl Siloxane, hexaorganodisiloxanes, such as hexamethyldisiloxane, divinyltetramethyldisiloxane; hexaorganodisilazanes, such as hexamethyldisilazane (HMDZ), divinyltetramethyldisilazane and tetramethyldi(trifluoropropyl)disilazane; hydroxyldimethyl terminated polydimethylmethylvinyl siloxane, octamethyl cyclotetrasiloxane, and silanes including but not limited to methyltrimethoxysilane, dimethyldimethoxysilane, vinyltrimethoxysilane, methyltriethoxysilane, vinyltriethoxysilane, chlorotrimethyl silane, dichlorodimethyl silane, trichloromethyl silane.

The surface treatment of the fillers makes them easily wetted by component (a). These surface modified fillers are preferably in a finely divided form and do not clump and can be homogeneously incorporated into the silicone polymer (a) This results in improved room temperature mechanical properties of the uncured compositions. The fillers may be pre-treated or may be treated in situ when being mixed with component (a). A small amount of water can be added together with the silica treating agent(s) as processing aid.

Depending on the filler(s) chosen, the fillers (d') are present in an amount of from 2.5 to 60 % by weight (wt. %) of the one-part condensation curable silicone composition described herein. In the case when the selected fillers are precipitated silica and/or fumed silica or a combination thereof the fillers (d') are present in a range of from about 5.0 to 35 wt. % of the composition, alternatively of from 5 to 30 wt. % of the composition, alternatively of from 5 to 25 wt. % of the composition. However, when filler (d') is precipitated calcium carbonate, the composition will tend to include a larger wt. % of the composition, e.g., from 25 to 60 wt. % of the composition, alternatively of from 30 to 60 wt. % of the composition, alternatively of from 35 to 55 wt. % of the composition. When component (d') is a mixture of silica and precipitated calcium carbonate the wt. % will typically somewhere therebetween.

The moisture content of filler(s) was determined by measurement using a Mettler Toledo Halogen Moisture Analyzer Model HR83 using the process described above.

Optional Additives

Optional additives may be used if required necessary. These may include non-reinforcing fillers, adhesion promoters, pigments and colourants, rheology modifiers, cure modifiers, plasticisers and/or extenders and fungicides and/or biocides and the like; It will be appreciated that some of the additives may be included in more than one list of additives. Such additives would then have the ability to function in all the different ways referred to.

Non-reinforcing fillers which may be hydrophobically treated.

Non-reinforcing fillers, which might be used in addition to the fillers identified as component (d') herein include aluminite, calcium sulphate (anhydrite), gypsum, nepheline, syenite, quartz, calcium sulphate, magnesium carbonate, ground calcium carbonate, clays such as kaolin, aluminium trihydroxide, magnesium hydroxide (brucite), graphite, copper carbonate, e.g., malachite, nickel carbonate, e.g., zarachite, barium carbonate, e.g., witherite and/or strontium carbonate e.g., strontianite; 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; $3Al_2O_3.2SiO_2$; kyanite; and Al_2SiO_5.

They may also include ring silicates which comprise silicate minerals, such as but not limited to, cordierite and $Al_3(Mg,Fe)_2[Si_4AlO_{18}]$ and chain silicates which are silicate minerals, such as but not limited to, wollastonite and $Ca[SiO_3]$.

Sheet silicates may also be utilised if desired such as but not limited to, mica; $K_2AI_{14}[Si_6Al_2O_{20}](OH)_4$; 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.

Such additional fillers may also be hydrophobically treated in the same manner as component (d') as described above. When present the non-reinforcing fillers tend to be used to replace some of component (d'), hence when component (d') is precipitated calcium carbonate and a non-reinforcing filler is also present in the composition the total amount of precipitated calcium carbonate and non-reinforcing filler will still be no more than the upper limit 60 wt. % of the composition. When present the non-reinforcing filler may be present in an amount of from greater than zero to 20 wt. % of the composition.

Adhesion promoters

The one-part condensation curable silicone composition as hereinbefore described may also comprise one or more suitable adhesion promoters. For the avoidance of doubt said adhesion promoter(s) is/are different from cross-linker (b). For example, the adhesion promoter may be selected from one or more mercaptopropyltrialkoxysilanes, an aminopropyltriethoxysilane, an aminopropyltrimethoxysilane or an amine of the structure:

$$R^{20}_k(R^{21}O)_{3-k}Si\text{-}Z^1\text{-}N(H)\text{-}(CH_2)_m\text{-}NH_2$$

in which R^{20} is an alkyl group containing from 1 to 10 carbon atoms; each R^{21} may be the same or different and is H or R^{20}, Z^1 is a linear or branched alkylene group having from 2 to 10 carbon atoms, m is from 2 to 10 and k is zero or 1.

R^{20} is an alkyl group containing from 1 to 10 carbon atoms, alternatively R^{20} is an alkyl group containing from 1 to 6 carbon atoms, alternatively,

R^{20} is a methyl or ethyl group. Each R^{21} may be the same or different and is H or R^{20}, alternatively each R^{21} is R^{20}. In one alternative all R^{21} groups are the same. When the R^{21} groups are the same, it is preferred that they are methyl or ethyl groups.

Z^1 is a linear or branched alkylene group having from 2 to 10 carbons, alternatively from 2 to 6 carbons, for example Z^1 may be a propylene group, a butylene group or an isobutylene group. There may be from 2 to 10 m groups, in one alterative m may be from 2 to 6, in another alternative m may be from 2 to 5, in a still further alternative m may be 2 or 3, alternatively m is 2.

Specific examples include but are not limited to aminopropyltriethoxysilane, aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminoisobutylmethyldimethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl)-2-aminoethylmethyldimethoxysilane, N-(2-aminoethyl)-3-aminoisobutylethyldimethoxysilane, N-(2-aminoethyl)-2-aminoethylmethyldimethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyldiethoxysilane, N-(2-aminoethyl)-2-aminoethylmethyldiethoxysilane, N-(2-aminoethyl)-3-aminoisobutylethyldiethoxysilane, N-(2-aminoethyl)-2-aminoethylmethyldiethoxysilane, N-(2-aminoethyl)-3-aminopropylmethylmethoxyethoxysilane, N-(2-aminoethyl)-2-aminoethylmethylmethoxyethoxysilane, N-(2-aminoethyl)-3-aminoisobutylethylmethoxyethoxysilane, N-(2-aminoethyl)-2-aminoethylmethylmethoxyethoxysilane, N-(2-aminopropyl)-3-aminoisobutylmethyldimethoxysilane, N-(2-aminopropyl)-3-aminopropylmethyldimethoxysilane, N-(2-aminopropyl)-2-aminoethylmethyldimethoxysilane, N-(2-aminopropyl)-3-aminoisobutylethyldimethoxysilane, N-(2-aminopropyl)-2-aminoethylmethyldimethoxysilane, N-(2-aminopropyl)-3-aminopropylmethyldiethoxysilane, N-(2-aminopropyl)-2-aminoethylmethyldiethoxysilane, N-(2-aminopropyl)-3-aminoisobutylethyldiethoxysilane, N-(2-aminopropyl)-2-aminoethylmethyldiethoxysilane, N-(2-aminopropyl)-3-aminopropylmethylmethoxyethoxysilane, N-(2-aminopropyl)-2-aminoethylmethylmethoxyethoxysilane, N-(2-aminopropyl)-3-aminoisobutylethylmethoxyethoxysilane, N-(2-aminopropyl)-2-aminoethylmethylmethoxyethoxysilane as well as their trialkoxy, especially trimethoxy and triethoxy equivalents (where k is zero) such as 3-(2-aminoethyl)-aminopropyltriethoxysilane, 3-(2-aminoethyl)-aminopropyltrimethoxysilane, N-(3-(Trimethoxysilyl)propyl)butylamine and bis(trimethoxysilylpropyl)amine.

The adhesion promoter when present is present in an amount of from 0.05 to 3.75% by weight of the composition, alternatively, in an amount of 0.05- 2.5 % by weight of the composition, alternatively, in an amount of 0.05- 2.0 % by weight of the composition, alternatively, in an amount of 0.05 to 1.0 % by weight of the composition.

Pigments and/or colorants

The one-part condensation curable silicone composition as described herein may further comprise one or more pigments and/or colorants. The pigments and/or colorants may be coloured, white, black, metal effect, and luminescent e.g., fluorescent or phosphorescent. Pigments are utilized to colour the composition as required. Any suitable pigment may be utilized providing it is compatible with the composition herein. In one-part condensation curable silicone compositions pigments and/or coloured (non-white) fillers e.g., carbon black may be utilized in the catalyst package to colour the end sealant product.

Suitable white pigments and/or colorants include titanium dioxide, zinc oxide, lead oxide, zinc sulfide, lithophone, zirconium oxide, and antimony oxide.

Suitable non-white inorganic pigments and/or colorants include, but are not limited to, iron oxide pigments such as goethite, lepidocrocite, hematite, maghemite, and magnetite black iron oxide, yellow iron oxide, brown iron oxide, and red iron oxide; blue iron pigments; chromium oxide pigments; cadmium pigments such as cadmium yellow, cadmium red, and cadmium cinnabar; bismuth pigments such as bismuth vanadate and bismuth vanadate molybdate; mixed metal oxide pigments such as cobalt titanate green; chromate and molybdate pigments such as chromium yellow, molybdate red, and molybdate orange; ultramarine pigments; cobalt oxide pigments; nickel antimony titanates; lead chrome; carbon black (when present, carbon black will function as both a non-reinforcing filler and colorant); lampblack, and metal effect pigments such as aluminium, copper, copper oxide, bronze, stainless steel, nickel, zinc, and brass.

Suitable organic non-white pigments and/or colorants include phthalocyanine pigments, e.g., phthalocyanine blue and phthalocyanine green; monoarylide yellow, diarylide yellow, benzimidazolone yellow, heterocyclic yellow, DAN orange, quinacridone pigments, e.g., quinacridone magenta and quinacridone violet; organic reds, including metallized azo reds and nonmetallized azo reds and other azo pigments, monoazo pigments, diazo pigments, azo pigment lakes, β-naphthol pigments, naphthol AS pigments, benzimidazolone pigments, diazo condensation pigment, isoindolinone, and isoindoline pigments, polycyclic pigments, perylene and perinone pigments, thioindigo pigments, anthrapyrimidone pigments, flavanthrone pigments, anthanthrone pigments, dioxazine pigments, triarylcarbonium pigments, quinophthalone pigments, and diketopyrrolo pyrrole pigments.

Typically, the pigments and/or colorants, when particulates, have average particle diameters in the range of from 10 nm to 50 μm, preferably in the range of from 40 nm to 2 μm. The pigments and/or colorants when present are present in the range of from 2, alternatively from 3, alternatively from 5 to 20 wt. % of the composition.

Rheology modifiers

Rheology modifiers which may be incorporated in the one-part condensation curable silicone composition include silicone organic co-polymers such as those described in EP0802233 based on

polyols of polyethers or polyesters; non-ionic surfactants selected from the group consisting of polyethylene glycol, polypropylene glycol, ethoxylated castor oil, oleic acid ethoxylate, alkylphenol ethoxylates, copolymers or ethylene oxide and propylene oxide, and silicone polyether copolymers; as well as silicone glycols. For some systems these rheology modifiers, particularly copolymers of ethylene oxide and propylene oxide, and silicone polyether copolymers, may enhance the adhesion to substrates, particularly plastic substrates.

UV and/or light stabilizers

UV and/or light stabilizers may include, for the sake of example include benzotriazole, ultraviolet light absorbers and/or hindered amine light stabilizers (HALS) such as the TINUVIN® product line from Ciba Specialty Chemicals Inc.

Plasticisers and Extenders

The composition as hereinbefore described may comprise a plasticizer or extender (sometimes referred to as a processing aid) in the form of a silicone or organic fluid which is unreactive with organopolysiloxane polymer(s) (a) and/or crosslinker(s) (b) and/or titanium-based reaction product (c), whether otherwise reactive or unreactive. If present the plasticizer or extender content will be present in an amount of from 5 to 30 wt. % of the composition, alternatively from 5 to 10 wt. % or the composition.

Examples of non-reactive silicone fluids useful as plasticizers include polydiorganosiloxanes such as polydimethylsiloxane having terminal triorganosiloxy groups wherein the organic substituents are, for example, methyl, vinyl or phenyl or combinations of these groups. Such polydimethylsiloxanes can for example have a viscosity of from about 5 to about 100,000 mPa.s at 25°C.

Alternatively compatible organic plasticisers may be utilised additionally to or instead of the silicone fluid plasticiser include dialkyl phthalates wherein the alkyl group may be linear and/or branched and contains from six to 20 carbon atoms such as dioctyl, dihexyl, dinonyl, didecyl, diallanyl and other phthalates, and analogous adipate, azelate, oleate and sebacate esters; polyols such as ethylene glycol and its derivatives; and organic phosphates such as tricresyl phosphate and/or triphenyl phosphates.

Examples of extenders for use in compositions herein include mineral oil based (typically petroleum based) paraffinic hydrocarbons, mixtures of paraffinic and naphthenic hydrocarbons, paraffin oils comprising cyclic paraffins and non-cyclic paraffins and hydrocarbon fluids containing naphthenics, polycyclic naphthenics and paraffins, or polyalkylbenzenes such as heavy alkylates (alkylated aromatic materials remaining after distillation of oil in a refinery). Examples of such extenders are discussed in GB2424898 the content of which is hereby enclosed by reference.

Biocides

Biocides may additionally be utilized in the composition if required. It is intended that the term "biocides" includes bactericides, fungicides and algicides, and the like. Suitable examples of useful

biocides, which may be utilized in compositions as described herein, include, for the sake of example:

Carbamates such as methyl-N-benzimidazol-2-ylcarbamate (carbendazim) and other suitable carbamates, 10,10'-oxybisphenoxarsine, 2-(4-thiazolyl)-benzimidazole, N-(fluorodichloromethylthio)phthalimide, diiodomethyl p-tolyl sulfone, if appropriate in combination with a UV stabilizer, such as 2,6-di(tert-butyl)-p-cresol, 3-iodo-2-propinyl butylcarbamate (IPBC), zinc 2-pyridinethiol 1-oxide, triazolyl compounds and isothiazolinones, such as 4,5-dichloro-2-(n-octyl)-4-isothiazolin-3-one (DCOIT), 2-(n-octyl)-4-isothiazolin-3-one (OIT) and n-butyl-1,2-benzisothiazolin-3-one (BBIT). Other biocides might include for example Zinc Pyridinethione, 1-(4-Chlorophenyl)-4,4-dimethyl-3-(1,2,4-triazol-1-ylmethyl)pentan-3-ol and/or 1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl] methyl]-1H-1,2,4-triazole.

The fungicide and/or biocide may suitably be present in an amount of from greater than 0 to 0.3wt. % of the composition and may be present in an encapsulated form where required such as described in EP2106418.

Hence, the one-part condensation curable silicone composition which is suitable for use in humid climates i.e., hot and damp climates having high temperatures (e.g., greater than or equal to (≥) 30°C) and high relative humidity (RH) (e.g., greater than or equal to 75% RH) as described herein may comprise:

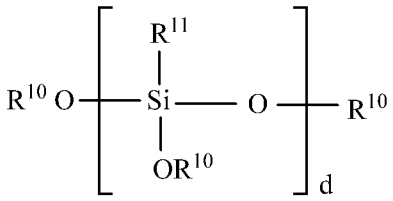
(a) an organopolysiloxane polymer having at least two hydrolysable groups per molecule (a) described above of the formula:

$$X_{3-n}R_nSi\text{-}Z\text{-}(R^1{}_ySiO_{(4-y)/2})_z\text{–}SiR^1{}_2\text{-}Z\text{-}Si\text{-}R_nX_{3-n} \quad (1)$$

in which each X is independently a hydrolysable group, alternatively an alkoxy group, each R is an alkyl, alkenyl or aryl group, each R^1 is an X group or an R group, alternatively an X group, an alkyl group or an aryl group, alternatively an X group or an alkyl group and each Z may be the same or different and is oxygen or a divalent organic group;

n is 0, 1, 2 or 3; y is 0, 1 or 2, preferably 2 and z is an integer such that said organopolysiloxane polymer has a viscosity of from 10,000 to 150,000 mPa.s at 25°C, alternatively from 30,000 to 140,000mPa.s at 25°C, therefore z is an integer of from approximately 300 to 2000, wherein the organopolysiloxane polymer (a) described above is present in the composition in an amount of from 30 to 90 weight % (wt. %) of the composition, alternatively, 30 to 80 wt. % of the composition alternatively 35 to 75 wt. % of the composition, alternatively 35 to 60 wt. % of the composition;

(b) a cross-linker of the structure:



Wherein each R^{10} may be the same or different and is an alkyl group having from 1 to 8 carbons, and each R^{11} is an alkenyl group having from 2 to 8 carbons and d is from 1 to 10. Preferably component (b) is a trialkoxyalkenyl silane where d is 1 but it may be an oligomer thereof where d is from 2 to 10 and is present in a range of from 1 to 10 wt. % of the one-part condensation curable silicone composition curable silicone composition, alternatively from 1.25 to 7.5 weight % of the composition, alternatively from 1.5 to 5.0 weight % of the composition;

c) is a titanium-based reaction product as described above, obtained or obtainable from a process comprising the steps of:

(i) mixing a first ingredient, an alkoxy titanium compound having from 2 to 4 alkoxy groups with a second ingredient, a linear or branched polydiorganosiloxane polymer having at least two terminal silanol groups per molecule;

(ii) enabling the first and second ingredients to react together by stirring under vacuum to form a reaction product; and

collecting the reaction product of step (ii); and

(d') a filler comprising one or more of precipitated calcium carbonate, ground calcium carbonate, precipitated silica, fumed silica or a mixture thereof which filler has been hydrophobically treated and is preferably provided in a finely divided form wherein the surface area is at least 15 m^2/g in the case of ground and/or precipitated calcium carbonate measured in accordance with the BET method (ISO 9277: 2010), alternatively 15 to 50 m^2/g, alternatively 15 to 25 m^2/g and at least 50 m^2/g in accordance with the BET method (ISO 9277: 2010) in the case of high surface area fumed silica and/or high surface area precipitated silica, measured in accordance with the BET method (ISO 9277: 2010), and depending on the filler(s) chosen, the fillers (d') are present in an amount of from 2.5 to 60 % by weight (wt. %) of the one-part condensation curable silicone composition described herein as discussed previously. A further requirement is that the molar ratio of OH groups : alkoxy groups is in the range of from 0.09 : 1 to 0.1375 : 1.

The one-part condensation curable silicone composition may comprise any combination of the above providing that the total composition of ingredients (a) to (d') together with any other optional ingredients included in the composition has a value of 100 wt. % of the composition.

There is also provided a method for preparing a one-part silicone composition curable at a temperature of at least 30° C and greater than relative humidity of 75 % determined using a hygrometer by first preparing the titanium-based reaction product (c) as described above and collecting the reaction product before mixing said titanium-based reaction product (c) with components (a), (b) and (d') in any suitable order. There are a wide range of hygrometers which can be used, as described above. An EXTECH humidity and temperature recorder, Model RH520 commercially available from the Extech Instrumentation Corporation was preferred.

For example, the titanium-based reaction product (c) may be prepared in a suitable mixer and or compounder by mixing a dimethylsilanol terminated polydimethylsiloxane having a viscosity of ca

500 to 2000 mPa.s at 25°C after which an appropriate amount of a tetraalkoxy titanium compound is added. The resulting combination is mixed together at a low speed but with a dissolver disc rotating at high speed to induce high shear mixing for a period of between 1 and 10 minutes. Any gel which forms during the formation of titanium-based reaction product (c) during the reaction is removed. The resulting mixture is mixed again for a further period of 1 to 10 minutes in the same or an alternative mixer whilst gradually increasing the speed of the mixer after which vacuum can be applied and once a predefined temperature of between 75 and 115°C has been reached by way of shear mixing and the mixture is reacted for a further period of time which is at least 30 minutes, alternatively at least 60 minutes at the elevated temperature under vacuum after which the resulting titanium-based reaction product (c) is allowed to cool and is collected.

The titanium-based reaction product (c) resulting from the above reaction is then mixed with the component (a), (b) and (d') in any suitable order to form the composition herein.The one-part alkoxy curing prototype is made via the follow steps. For example, once titanium-based reaction product (c) has been obtained by the above reaction component (a) may be introduced into the component (c) reaction product and then is mixed, optionally under vacuum for several minutes, after which component (b) the cross-linker is added and mixed in, again optionally under vacuum with components (a) and (c), after which filler component (d') was added and intermixed with the other ingredients and the final mixture was missed under vacuum to remove as much moisture as possible.

As previously discussed, one-part silicone sealant compositions are traditionally slow curing because they rely on skin or diffusion cure (e.g., moisture/condensation) which takes place by the formation of a cured skin at the composition/air interface subsequent to the sealant/encapsulant being applied on to and/or between one or more substrates. It involves the diffusion of moisture from the sealant/encapsulant interface with air to the inside (or core) of the layer of silicone composition applied, the diffusion of condensation reaction by-product/effluent from the inside (or core) to the outside (or surface) of the curing material and the gradual thickening of the cured skin over time from the outside/surface to the inside/core. Furthermore, whilst moisture is required to initiate cure, its presence especially in hot humid climates can result in the tetra alkyl titanate catalysts fully hydrolysing to tetra alkyl titanate catalysts to form titanium (IV) hydroxide ($Ti(OH)_4$). These compounds only have a limited solubility in silicone-based compositions, often resulting in a dramatic decrease in catalytic efficiency of the titanium-based compound(s) for curing condensation curable silicone compositions, consequently leading to even slower skin curing process than at room temperature in hot and humid situations with the alkoxy titanium present at the sealant/air interface of the curing sealant being fully hydrolysed, resulting in a highly tacky surface, while the bulk of the sealant may eventually cure normally as the moisture penetrates the curing sealant.

Surprisingly it was found that the utilisation of component (c) instead of the standard titanate and/or zirconate catalysts enables the use of a titanium-based catalyst in a one-part silicone sealant composition in hot and humid climates and does not result in a tacky air/sealant interface.

Additionally, it was surprisingly identified that by having have a molar ratio of OH groups : alkoxy groups in the composition in the range of from 0.09 : 1 to 0.1375 : 1 enabled a sealant with an acceptable tack free time (TFT) (i.e., preferably from 30-240min measured in accordance with ASTM C679)to be generated upon cure and a stable one-part composition herein which is storage stable for at least 4 months, alternatively at least 5 months, alternatively at least 6 months was obtained.

It was found that to ensure an acceptable tack free time (TFT) (30-240 minutes measured in accordance with ASTM C679) a molar ratio of OH groups : alkoxy groups of at least 0.09 : 1 was required. It was also identified that a molar ratio of OH groups : alkoxy groups of at most 0.1375 : 1 was required to ensure a stable one-part composition herein which is storage stable for at least 4 months, alternatively at least 5 months, alternatively at least 6 months. When the ratio was greater than 0.1375 : 1 the composition became increasingly unstable in storage. Hence, by using titanium-based reaction product (c) herein instead of standard titanate and zirconate catalysts a one part titanium-based reaction product (c) catalysed composition can be utilised in e.g., hot and humid environments/climates, i.e., where the temperature is regularly above 30°C with a relative humidity of at least 75% as titanium-based reaction product (c) does not appear to have the same level of sensitivity because to hydrolysis (e.g., the cleavage of bonds of functional groups by reaction with water) especially at elevated temperatures and as such do not liberate the corresponding alcohol with respect to the alkoxy group(s) bound to the titanium. This means that a suitable alternative has been found for both standard titanates and zirconates at elevated temperatures and high humidity as well as to tin cured condensation systems as such a titanium material as titanium-based reaction product (c) will not cause and/or undergo reversion (i.e., depolymerisation) at temperatures above 80°C and in a humid environment. Silicone sealant compositions as described herein are also stable for several months which is an additional advantage over tin (IV) catalysed compositions which are known in the industry to be difficult to stabilize for a long storage period and as such a solution for a one-part silicone sealant with an acceptable curing (e.g., resulting in a TFT of from 30-240 minutes measured in accordance with ASTM C679 as mentioned above) suitable for use in climates regularly having elevated temperatures and high humidity such as on the Indian and African continents is provided.

Such a development will be very helpful for the building who have a preference to use one-part sealants as they are more convenient for structural bonding applications of glass and metal in factory or field situations and in this case is particularly designed for use in silicone structural glazing (SSG) in areas subjected to extremely hot temperatures such as up to at 80°C or higher.

Preferably the composition herein is gunnable (i.e., it is suitable to be applied on a target using a sealant gun apparatus). Hence, the one-part condensation curable silicone composition as hereinbefore described may be a gunnable sealant composition used for

(i) space/gap filling applications;

(ii) sealing applications, such as sealing the edge of a lap joint in a construction membrane; or

(iii) a stain-resistant weather sealing sealant;

(iv) adhering at least two substrates together; and/or

In the case of the one-part condensation curable silicone composition as hereinbefore described, there is provided a method for filling a space between two substrates so as to create a seal therebetween, comprising:

a") providing a one-part condensation curable silicone composition as hereinbefore described, and either:

b") applying the one-part condensation curable silicone composition on to a first substrate, and bringing a second substrate in contact with the silicone composition that has been applied to the first substrate wherein either or both of said substrates are porous substrates at a temperature of at least 40°C, or

c") filling a space formed by the arrangement of a first substrate and a second substrate wherein either or both of said substrates are porous substrates at a temperature of at least 40°C, with the one-part condensation curable silicone composition and

d") curing same.

The product of the composition as hereinbefore described may be utilised for formulating sealants, adhesives, e.g. structural adhesives and pressure sensitive adhesives, encapsulants, pottants, coatings, pressure sensitive adhesives, cured articles for use in construction applications e.g. spacers for glass, automotive applications, electronics applications, e.g. electrically conductive materials, crystal clear materials for LEDs, pottants for solar, electronics and optical devices. displays and optical applications, solar applications, personal care e.g., hair care, skin care and health care applications.

Examples

A series of examples are now provided.

All viscosity measurements were taken at 25°C unless otherwise indicated. Unless otherwise indicated, all viscosities in the examples were measured in accordance with the ASTM D4287 Cone and Plate Method using a Brookfield DV-III Ultra Rheometer.

Several examples of the titanium-based reaction product (c) were prepared but for the sake of comparison titanium-based reaction product (c) 1 was utilised in the following Examples:

Preparation of titanium-based reaction product (c) 1

Titanium-based reaction product (c) 1 was prepared using a Neulinger 50-liter compounder. 19058 g of dimethylsilanol terminated polydimethylsiloxane having a viscosity of ca 800 mPa.s at 25°C was first loaded into the compounder. 76.232 g of tetraisopropoxy titanium was then introduced into the compounder and was mixed for 2 minutes at low speed using a dissolver disk mixing element to induce high shear. A small amount of gel was accumulated on the dissolver disk and removed with a spatula. The resulting mixture was then mixed for another 2 minutes using a planetary mixing element and the dissolver disk mixing element with both the using a planetary mixing element and the speed d was slowly increased to 50 rpm for the planetary mixing element and 1300 rpm on the dissolver mixing element. Vacuum was then applied and the temperature was raised by shear mixing to 90°C. The resulting mixture was further mixed under dynamic vacuum for about 90 minutes. The measured final viscosity was 23,275 mPa.s at 25°C using a Modular compact rheometer (MCR 302 from Anton Paar GmbH of Graz, Austria using a 25mm diameter rational plate with a gap of 0.3mm at a shear rate of $1s^{-1}$.

Preparation of titanium-based reaction product (c) 2

A component (c) titanium-based reaction product was the first prepared. 200g of dimethylsilanol terminated polydimethylsiloxane having a viscosity of 2,163 mPa.s at 25°C was introduced into a plastic receptacle of a DAC 600 FVZ/VAC-P type SpeedMixer™ from Hauschild. 0.497g of tetraisopropoxy titanium were then added into the dimethylsilanol terminated polydimethylsiloxane. A lid was placed on the receptacle and the initial weight of the ingredients, the receptacle and the lid were weighed together.

The ingredients were then mixed in the Hauschild DAC 600 FVZ/VAC-P SpeedMixer™ for 2 minutes at 2350 rpm at atmospheric pressure and then 2 minutes at 2350 rpm under vacuum and then left 6 minutes under vacuum without mixing. This mixing regime was repeated.

The viscosity of the reaction product generated via the above process was determined to be 47,338 mPa.s using a Modular Compact Rheometer (MCR) 302 from Anton Paar GmbH of Graz, Austria using a 25mm diameter rotational plate with a gap of 0.3 mm at a shear rate of $1s^{-1}$.

The above are merely examples for making the component (c) titanium-based reaction product further examples thereof are described in the examples 2 onwards in WO2022108893A1 and are incorporated herein by reference. However, for the following examples titanium-based reaction product (c) 1 was utilised.

The compositions of examples 1 to 4 (Ex. 1 to 4) and comparatives 1 to 3 (C. 1 – C. 3) are provided in Table 1a and the compositions of Ex. 5 to 7 and C. 4 and 5 and are provided below in Table 2a.

Table 1a: Compositions of examples 1 to 4 (Ex. 1 to 4) and comparatives 1 to 3 (C. 1 – C. 3) (wt. %)

	C. 1	**C. 2**	**Ex. 1**	**Ex. 2**	**Ex. 3**	**Ex. 4**	**C. 3**
Ti-based reaction product (c) 1	15	20	15	20	25	30	30
Polymer 1	40	35	40	35	30	25	20
MTM X-linker	3	3					
VTM X-linker			3	3	3	3	3
GCC filler	42	42	42	42	42	42	47
Total	100	100	100	100	100	100	100

In Table 1a:

Ti-based reaction product (c) 1 was the product resulting from the method described above;

Polymer 1: Polymer 1 was a polydimethylsiloxane polymer terminated with $(MeO)_3$ Si-CH_2-CH_2- terminal groups and having a viscosity of approximately 65,000mPa.s at 25°C;

MTM X-linker was methyl trimethoxysilane;

VTM X-linker was vinyl trimethoxysilane; and

Ground calcium carbonate (GCC): The GCC was Omyabond™ 120-FO which is a low moisture, ultrafine, treated, ground calcium carbonate (GCC) commercially available from OMYA AG, having a median particle size d50% (Omya GLS 041, Sedigraph) of 0.3µm and a specific surface area BET (Omya GLS 067) of 14m^2/g (taken from technical data sheet).

The moisture content in the ground calcium carbonate used in the examples was found to be approximately 0.191% and was determined as described above using a Mettler Halogen Moisture Analyzer Model HR83 by determining the weight of the filler powder before and after being heated at 105°C for 20 minutes and the wt. % of water present was determined from the difference.

The pertinent ratios of the contents of examples 1 to 4 (Ex. 1 to 4) and comparatives 1 to 3 (C. 1 – C. 3) are provided in Table 1b below:

Table 1b: Molar Content and Ratios of the components in Ex. 1 to 4 and C. 1 – C. 3

	C. 1	C. 2	Ex. 1	Ex. 2	Ex. 3	Ex. 4	C. 3
Ti content (mmol)	0.215	0.286	0.215	0.286	0.358	0.429	0.429
-OH (mmol)	6.253	6.851	6.253	6.851	7.450	8.049	8.579
MeO (mmol)	68.130	67.872	62.777	62.519	62.262	62.004	61.746
-OH : MeO	0.092 : 1	0.101 : 1	0.10 : 1	0.11 : 1	0.12 : 1	0.13 : 1	0.139 : 1

Table 1c below shows the sealant appearance/status when freshly made (fresh) as well as 3.5 months after having been made to assess storage stability. The samples were stored in a closed sealant cup (i.e., not as airtight as in a cartridge or aluminium foil sausage. Tack free Time relates to the cure

of fresh samples having been removed from the mixing cup and allowed to cure at room temperature.

Tack free time (TFT) was measured via polyethylene contact in accordance with ASTM C679 with the results are provided for cured fresh samples measured in minutes.

Table 1c: Storage stability of Ex. 1 to 4 and C. 1 – C. 3 after cure in room temperature (23~25°C) conditions with humidity not controlled

	C. 1	C. 2	Ex. 1	Ex. 2	Ex. 3	Ex. 4	C. 3
Sealant appearance, Fresh	Good	Good	Good	Good	Good	Good	Good
Tack free time (fresh), min	>300	160	>300	299	235	180	163
Sealant appearance, after 3.5M RT	Sticky	Very sticky	Good	Good	Good	A little sticky	Sticky

The samples assessed, in Table 1c, were just kept in a closed mixing cup at room temperature and pressure for 3.5 months and that uncured Ex. 1 – 3 were not sticky to the touch indicating a Ti-based reaction product (c) 1, polymer 1 and VTM composition remained storage stable it was deemed that in a sealed cartridge or aluminium foil sausage they would be storage stable for several months longer (from past experience). Ex. 4 showed a minor level of stickiness but was deemed to have a sufficiently satisfactory storage stability for use for an extended period of time of greater than four months if stored in a sealed cartridge or aluminium foil sausage. It was found that in C. 1 and C. 2 the sealant became very sticky in after 3.5 months and it was found similarly sticky in respect of C. 3 which had a molar ratio relationship of -OH : MeO of 0.139 : 1. It was also apparent the cross-linker needed to be component (b) as described herein rather than alternatives such as methyltrimethoxysilane which worked less well. Fresh samples of compositions utilised for each example and comparative example were then applied onto a glass substrate and then cured at 23°C and 50% relative humidity at a constant temperature in an LH-113 model humidity chamber from ESPEC Corporation of Osaka, Japan. These samples were applied onto glass substrates and then cured at 38°C and 95% RH chamber. The tack free time and surface tackiness were checked accordingly.

A Second series of examples (Ex. 5 to 7) and comparatives (C. 4 and C. 5) were prepared and similarly analysed. The compositions used are depicted in Table 2a below:

Table 2a: Compositions of Ex. 5 to 7, C. 4 and C5

	Ex. 5	**Ex. 6**	**Ex. 7**	**C. 4**	**C. 5**
Ti-based reaction product (c) 1	40	45	50		
TtBt				0.243	
TDIDE					0.303
Polymer 2				39.757	39.697
Polymer 1	30	32	30	30	30
VTM	3	3	3	3	3
GCC	27	20	17	17	17
Total	100	100	100	100	100

The components listed are as described previously or are identified below:

TtBt is tertary t-butyl titanate;

TDIDE was Tyzor™ PITA SM which is an 80:20 wt. % mixture of Diisopropoxy-bisethylacetoacetatotitanate and methyltrimethoxy silane and is commercially available from Dorf Ketal Speciality Catalysts LLC of Texas USA; and

Polymer 2 Polymer 2 dimethylhydroxy terminated polydimethylsiloxane having a viscosity of 2000mPa.s at 25°C.

The pertinent ratios of the contents of examples 1 to 4 (Ex. 1 to 4) and comparatives 1 to 3 (C. 1 – C. 3) are provided in Table 1b below:

Table 2b: Formulation and Performance of Example 8-11 and Comparative Example 1-2

	Ex. 5	Ex. 6	Ex. 7	C. 4	C. 5
-OH (mmol)	7.654	7.510	7.791	6.841	6.835
MeO (mmol)	62.262	62.365	62.262	62.262	62.262
-OH : MeO	0.123 : 1	0.120 :	0.125 : 1	0.11 : 1	0.11 : 1

Once prepared the compositions were allowed to cure at room temperature (23 – 25°C) and 50% relative humidity (RH) with tack free time being identified and the cured sealant appearance was checked after 5 hours of curing to assess whether or not tackiness was present and the results are provided in Table 2c below.

Table 2c: Performance of Ex. 5 to 7, C. 4 and C. 5 at room temperature and 50% relative humidity

	Ex. 5	Ex. 6	Ex. 7	C. 4	C. 5
Tack free time (minutes)	190	190	136	280	160
Cured sealant tackiness after 5hrs of curing	None	None	None	Very	A little

It will be seen that Ex. 5 to 7 each had a much faster TFT than both C. 4. Even though a tack free time is reached in accordance with the testing method, a degree of tackiness remains in the case of C. 5 this was then retested after a set period of time to assess the change in tackiness (or not). Once prepared analogous samples of the compositions were cured at a temperature of 38°C and 95 % relative humidity at a constant temperature in an LH-113 model humidity chamber from ESPEC Corporation of Osaka, Japan with tack free time being identified and the cured sealant appearance was checked after 3 hours of curing to assess if tackiness was present and the results are provided in Table 2d below.

Table 2d: Performance of Ex. 5 to 7, C. 4 and C. 5 at 38°C and 95% relative humidity

	Ex. 5	Ex. 6	Ex. 7	C. 4	C. 5
Tack free time (min)	55	55	38	116	60
Cured sealant tackiness after 3hrs of curing	Smooth surface, no tackiness	Smooth surface, no tackiness	Smooth surface, no tackiness	Bubbling on surface, very tacky	Bubbling on surface, a little tacky

It was found that formulations with Ti-based reaction product (c) in the examples herein were more robust compared to standard titanate catalysts. When exposed to high humidity, the normal titanate catalysts were found to hydrolyse forming titanium dioxide (TiO_2) consequently losing their catalytic activity whilst Ti-based reaction product (c) components remained stable.Hence, compositions with Ti-based reaction product (c) 1 when curing at a temperature of 38°C and 95 % relative humidity for 3hrs, all showed dry smooth surfaces, whilst for compositions C. 4 and C. 5 containing TtBT or TDIDE as catalysts respectively, the sealant surface was tacky and indeed bubbling was also observed at higher temperatures. This is similar to the results in Table 2c above. It is well demonstrated that Ti-based reaction product (c) 1 could help improve the curing performance of one-part alkoxy sealant, which can help address the slow cure issue particularly in hot, humid tropical climates like India.

WHAT IS CLAIMED IS:

1. A one-part condensation curable silicone composition comprising:

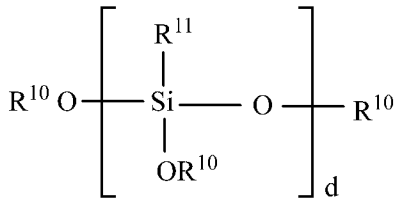
(a) an organopolysiloxane polymer of the formula

$X_{3-n}R_nSi\text{-}Z\text{-}(R^1{}_ySiO_{(4-y)/2})_z\text{–}SiR^1{}_2\text{-}Z\text{-}Si\text{-}R_nX_{3-n}$ (1)

in which each X is independently an alkoxy group, each R is an alkyl, alkenyl or aryl group, each R^1 is an X group, alkyl group, alkenyl group or aryl group and Z is oxygen or a divalent organic group;

n is 0 or 1, y is 0, 1 or 2, preferably 2 and z is an integer such that said organopolysiloxane polymer has a viscosity of from 10,000 to 150,000 mPa.s at 25°C, in an amount of from 30 to 80 weight % (wt. %) of the composition;

(b) a cross-linker of the structure:



Wherein each R^{10} may be the same or different and is an alkyl group having from 1 to 8 carbons, and each R^{11} is an alkenyl group having from 2 to 6 carbons and d is from 1 to 10;

(c) a titanium-based reaction product obtained or obtainable from a process comprising the steps of:

(i) mixing a first ingredient, an alkoxy titanium compound having from 2 to 4 alkoxy groups with a second ingredient, a linear or branched polydiorganosiloxane polymer having at least two terminal silanol groups per molecule;

(ii) enabling the first and second ingredients to react together by stirring under vacuum to form a reaction product; and

collecting the reaction product of step (ii); and

(d') a filler comprising one or more of precipitated calcium carbonate, ground calcium carbonate, precipitated silica, fumed silica or a mixture thereof which filler has been hydrophobically treated;

wherein the molar ratio of OH groups : alkoxy groups is in the range of from 0.09 : 1 to 0.1375 : 1.

2. A one-part condensation curable silicone composition in accordance with claim 1 wherein in component (a) and component (b) each n is zero and each Z is an alkylene having from 2 to 10 carbons.

3. A one-part condensation curable silicone composition in accordance with claim 1 or 2 wherein in component (b) each R^{10} is a methyl or ethyl group and each R^{11} is a vinyl, propenyl or hexenyl group.

4. A one-part condensation curable silicone composition in accordance with any preceding claim wherein the first ingredient in the method for the preparation of component (c) is $Ti(OR^5)_4$, $Ti(OR^5)_3R^6$, $Ti(OR^5)_2R^6{}_2$ or a chelated alkoxy titanium molecule where there are two alkoxy (OR^5)

groups present and a chelate bound twice to the titanium atom; where R^5 is a linear or branched alkyl group having from 1 to 20 carbons and each R^6 may be the same or different and is selected from an alkyl group, an alkenyl group or an alkynyl group in each case having up to 10 carbons.

5. A one-part condensation curable silicone composition in accordance with any preceding claim wherein the second ingredient in the method for the preparation of component (c) is a dialkylsilanol terminated polydimethylsiloxane.

6. A one-part condensation curable silicone composition in accordance with any preceding claim wherein the method for the preparation of component (c) utilises a third ingredient, a polydialkylsiloxane having one terminal silanol group per molecule is introduced in step (i).

7. A method for preparing a one-part condensation curable silicone composition comprising the steps of:

Preparing a titanium-based reaction product (c) with a process comprising the steps of:

(i) mixing a first ingredient, an alkoxy titanium compound having from 2 to 4 alkoxy groups with a second ingredient, a linear or branched polydiorganosiloxane polymer having at least two terminal silanol groups per molecule;

(ii) enabling the first and second ingredients to react together by stirring under vacuum to form a reaction product; and

collecting the reaction product of step (ii); and mixing said titanium-based reaction product (c) with the other components of the one-part silicone composition, namely:

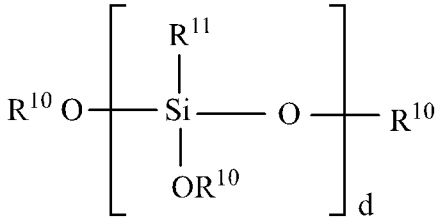
(a) an organopolysiloxane polymer of the formula

$$X_{3-n}R_nSi\text{-}Z\text{-}(R^1{}_ySiO_{(4-y)/2})_z\text{–}SiR^1{}_2\text{-}Z\text{-}Si\text{-}R_nX_{3-n} \quad (1)$$

in which each X is independently an alkoxy group, each R is an alkyl, alkenyl or aryl group, each R^1 is an X group, alkyl group, alkenyl group or aryl group and Z is oxygen or a divalent organic group;

n is 0 or 1, y is 0, 1 or 2, preferably 2 and z is an integer such that said organopolysiloxane polymer has a viscosity of from 10,000 to 150,000 mPa.s at 25°C, in an amount of from 30 to 80 weight % (wt. %) of the composition;

(b) a cross-linker of the structure:



Wherein each R^{10} may be the same or different and is an alkyl group having from 1 to 8 carbons, and each R^{11} is an alkenyl group having from 2 to 6 carbons and d is from 1 to 10;

and

(d') a filler comprising one or more of precipitated calcium carbonate, ground calcium carbonate, precipitated silica, fumed silica or a mixture thereof which filler has been hydrophobically treated;

wherein the molar ratio of OH groups : alkoxy groups is in the range of from 0.09 : 1 to 0.1375 : 1.

8. A method for preparing a one-part condensation curable silicone composition in accordance with claim 7 wherein the first ingredient in the method for the preparation of component (c) is $Ti(OR^5)_4$, $Ti(OR^5)_3R^6$, $Ti(OR^5)_2R^6_2$ or a chelated alkoxy titanium molecule where there are two alkoxy (OR^5) groups present and a chelate bound twice to the titanium atom; where R^5 is a linear or branched alkyl group having from 1 to 20 carbons and each R^6 may be the same or different and is selected from an alkyl group, an alkenyl group or an alkynyl group in each case having up to 10 carbons.

9. A method for preparing a one-part condensation curable silicone composition in accordance with claim 7 or 8 wherein the second ingredient in the method for the preparation of component (c) is a dialkylsilanol terminated polydimethylsiloxane.

10. A method for preparing a one-part condensation curable silicone composition in accordance with claim 7, 8 or 9 wherein the method for the preparation of component (c) utilises a third ingredient, a polydialkylsiloxane having one terminal silanol group per molecule is introduced in step (i).

11. A silicone material which is the cured product of the one-part condensation curable silicone composition in accordance with any one of claims 1 to 7 and/or the one-part condensation curable silicone composition made by the method in accordance with any one of claims 8 to 10.

12. A use of one-part condensation curable silicone composition comprising:

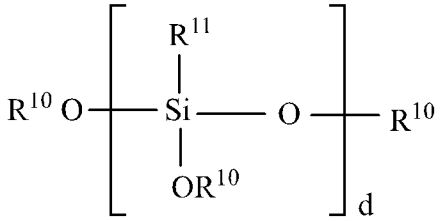
(a) an organopolysiloxane polymer of the formula

$$X_{3-n}R_nSi\text{-}Z\text{-}(R^1_ySiO_{(4-y)/2})_z\text{–}SiR^1_2\text{-}Z\text{-}Si\text{-}R_nX_{3-n} \quad (1)$$

in which each X is independently an alkoxy group, each R is an alkyl, alkenyl or aryl group, each R^1 is an X group, alkyl group, alkenyl group or aryl group and Z is oxygen or a divalent organic group;

n is 0 or 1, y is 0, 1 or 2, preferably 2 and z is an integer such that said organopolysiloxane polymer has a viscosity of from 10,000 to 150,000 mPa.s at 25°C, in an amount of from 30 to 80 weight % (wt. %) of the composition;

(b) a cross-linker of the structure:



Wherein each R^{10} may be the same or different and is an alkyl group having from 1 to 8 carbons, and each R^{11} is an alkenyl group having from 2 to 6 carbons and d is from 1 to 10;

(c) a titanium-based reaction product obtained or obtainable from a process comprising the steps of:

(i) mixing a first ingredient, an alkoxy titanium compound having from 2 to 4 alkoxy groups with a second ingredient, a linear or branched polydiorganosiloxane polymer having at least two terminal silanol groups per molecule;

(ii) enabling the first and second ingredients to react together by stirring under vacuum to form a reaction product; and

collecting the reaction product of step (ii); and

(d') a filler comprising one or more of precipitated calcium carbonate, ground calcium carbonate, precipitated silica, fumed silica or a mixture thereof which filler has been hydrophobically treated;

wherein the molar ratio of OH groups : alkoxy groups is in the range of from 0.09 : 1 to 0.1375 : 1;

as a one-part condensation curable silicone composition curable at a temperature of at least 30°C and greater than relative humidity of 75 % determined using a hygrometer.

13. Use of a titanium-based reaction product (c) obtained or obtainable from a process comprising the steps of:

(i) mixing a first ingredient, an alkoxy titanium compound having from 2 to 4 alkoxy groups with a second ingredient, a linear or branched polydiorganosiloxane polymer having at least two terminal silanol groups per molecule;

(ii) enabling the first and second ingredients to react together by stirring under vacuum to form a reaction product; and

collecting the reaction product of step (ii);

in a composition otherwise comprising:

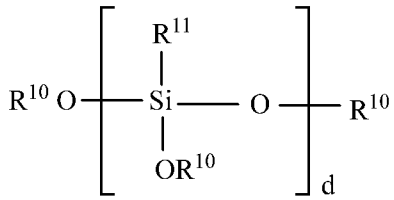
(a) an organopolysiloxane polymer of the formula

$X_{3-n}R_nSi\text{-}Z\text{-}(R^1{}_ySiO_{(4-y)/2})_z\text{–}SiR^1{}_2\text{-}Z\text{-}Si\text{-}R_nX_{3-n}$ (1)

in which each X is independently an alkoxy group, each R is an alkyl, alkenyl or aryl group, each R^1 is an X group, alkyl group, alkenyl group or aryl group and Z is oxygen or a divalent organic group;

n is 0 or 1, y is 0, 1 or 2, preferably 2 and z is an integer such that said organopolysiloxane polymer has a viscosity of from 10,000 to 150,000 mPa.s at 25°C, in an amount of from 30 to 80 weight % (wt. %) of the composition;

(b) a cross-linker of the structure:



Wherein each R^{10} may be the same or different and is an alkyl group having from 1 to 8 carbons, and each R^{11} is an alkenyl group having from 2 to 6 carbons and d is from 1 to 10;

and

(d') a filler comprising one or more of precipitated calcium carbonate, ground calcium carbonate, precipitated silica, fumed silica or a mixture thereof which filler has been hydrophobically treated;

wherein the molar ratio of OH groups : alkoxy groups is in the range of from 0.09 : 1 to 0.1375 : 1.

INTERNATIONAL SEARCH REPORT

International application No
PCT/CN2023/140779

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L83/04 C08K3/26 C09J183/04 C09D183/04 C08G77/16
C08G77/18 C08G77/50 C08G77/58
ADD.
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)
C08K C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 11 655 404 B2 (DOW SILICONES CORP [US]) 23 May 2023 (2023-05-23) examples 1-5 claims 1-16	1-13
A	WO 2022/108893 A1 (DOW SILICONES CORP [US]) 27 May 2022 (2022-05-27) examples 14, 15 tables 1-3	1-13
A	US 2023/391960 A1 (GUBBELS FREDERIC [BE]) 7 December 2023 (2023-12-07) tables 1-5	1-13
A	WO 2022/108894 A1 (DOW SILICONES CORP [US]) 27 May 2022 (2022-05-27) tables 1-9	1-13

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 May 2024	23/05/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Popescu, Teodora

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/CN2023/140779

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		WO 2022108894 A1	27-05-2022