

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
17 April 2008 (17.04.2008)

PCT

(10) International Publication Number
WO 2008/045446 A2

(51) International Patent Classification:
C08G 77/06 (2006.01) *C08L 83/07* (2006.01)
C08L 83/04 (2006.01)

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(21) International Application Number:
PCT/US2007/021588

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

(22) International Filing Date: 9 October 2007 (09.10.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/828,838 10 October 2006 (10.10.2006) US

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(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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Published:

— without international search report and to be republished upon receipt of that report

(54) Title: PROCESS FOR MAKING ORGANOPOLYSILOXANE COMPOSITIONS

(57) Abstract: A method for the production of an extended and/or plasticised silicone rubber compositions comprising the steps:- Mixing a polysiloxane containing polymer and/or precursors thereof with: - an extender and/or plasticiser prior to and/or during polymerisation of the polysiloxane containing polymer and/or Filler during or subsequent to polymerisation of the polysiloxane containing polymer and and optionally introducing residual extender and/or plasticiser and/or filler together with a first cure package for curing the polymer subsequent to polymerisation characterised in that the extender and/or plasticiser is chemically functionalised so as to substantially not participate in any chemical reaction(s) with the polymer and/or its precursors, prior to cure, but is chemically attached to the cross-linked matrix of the resulting cured elastomer during curing.



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PROCESS FOR MAKING ORGANOPOLYSILOXANE COMPOSITIONS

[0001] This invention is concerned with the use of plasticisers and extenders in silicone rubber based compositions.

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[0002] Organosiloxane compositions which cure to elastomeric solids are well known and such compositions can be produced to cure at either room temperature in the presence of moisture or with application of heat. Typically those compositions which cure at room temperature in the presence of moisture are obtained by mixing a polydiorganosiloxane based polymer having condensable terminal groups, with a suitable silane (or siloxane) based cross-linking agent in the presence of one or more fillers and a curing catalyst. These compositions are typically either prepared in the form of one-part compositions curable upon exposure to atmospheric moisture at room temperature or two part compositions curable upon mixing at room temperature and pressure.

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[0003] Such condensation cured compositions are commonly used as sealants in the construction and DIY markets. In use as a sealant, it is important that the composition has a blend of properties which render it capable of being applied as a paste to a joint between substrate surfaces where it can be worked, prior to curing, to provide a smooth surfaced mass which will remain in its allotted position until it has cured into an elastomeric body adherent to the adjacent substrate surfaces. Typically sealant compositions are designed to cure quickly enough to provide a sound seal within several hours but at a speed enabling the applied material to be tooled into a desired configuration shortly after application. The resulting cured sealant is generally formulated to have a strength and elasticity appropriate for the particular joint concerned.

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[0004] In view of the nature and use of many sealants as merely a means of filling gaps between e.g. a wall and a bath or sink or the like, the shrinkage of such sealant compositions during the curing process is typically not viewed as detrimental to the function of the resulting cured product and thus the introduction of additives which

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are unreactive with the silicone composition and which at least to an extent may evaporate during the curing of the sealant has become common practice in the sealants industry.

5 [0005] These additives are said to “extend” and/or “plasticise” the silicone sealant composition by blending the or each extending compound (henceforth referred to as an “extender”) and/or plasticising compound (henceforth referred to as a “plasticiser”) with a pre-prepared polymer and other ingredients of the composition.

10 [0006] An extender (sometimes also referred to as a process aid or secondary plasticiser) is used to dilute the sealant composition and basically make the sealant more economically competitive without substantially negatively affecting the properties of the sealant formulation. The introduction of one or more extenders into a silicone sealant composition not only reduces the overall cost of the product but can
15 also affect the properties of resulting uncured and/or cured silicone sealants. The addition of extenders can, to a degree, positively effect the rheology, adhesion tooling properties and clarity of a silicone sealant and can cause an increase in elongation at break and a reduction in hardness of the cured product both of which can significantly enhance the lifetime of the cured sealant provided the extender is not lost from the
20 cured sealant by, for example, evaporation or exudation.

[0007] A plasticiser (otherwise referred to as a primary plasticiser) is added to a sealant composition to provide properties within the final polymer based product to increase the flexibility and toughness of the final sealant composition. This is
25 generally achieved by reduction of the glass transition temperature (T_g) of the cured polymer composition thereby generally, in the case of sealants for example, enhancing the elasticity of the sealant which in turn enables movement capabilities in a joint formed by a silicone sealant with a significant decrease in the likelihood of fracture of the bond formed between sealant and substrate when a sealant is applied
30 thereto and cured. Plasticisers are typically used to also reduce the modulus of the sealant formulation. Plasticisers may reduce the overall unit cost of a sealant but that is not their main intended use and indeed some plasticisers are expensive and could

increase the unit cost of a sealant formulation in which they are used. Plasticisers tend to be generally less volatile than extenders and are typically introduced into the polymer composition in the form of liquids or low melting point solids (which become miscible liquids during processing).

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[0008] Typically, for silicone based, condensation cure, compositions, which are generally used in sealant compositions, plasticisers are organopolysiloxanes which are unreactive with the siloxane polymer of the composition, 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 normally have a viscosity of from about 5 to about 100,000 mPa.s at 25°C. Compatible organic plasticisers may additionally be used, examples 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; adipate, azelate, oleate and sebacate esters, polyols such as ethylene glycol and its derivatives, organic phosphates such as tricresyl phosphate and/or triphenyl phosphates.

[0009] A wide variety of organic compounds and compositions have been proposed for use as extenders for reducing the cost of the silicone sealant compositions. Whilst polyalkylbenzenes such as heavy alkylates (alkylated aromatic materials remaining after distillation of oil in a refinery) have been proposed as extender materials for silicone sealant compositions in recent years the industry has increasingly used mineral oil based (typically petroleum based) paraffinic hydrocarbons as extenders as described in GB 2424898 which was published after the priority date of this application and the following publications: EP0885921 describes the use of mineral oil based hydrocarbon mixtures containing 60 to 80% paraffinic and 20 to 40% naphthenic and a maximum of 1% aromatic carbon atoms. EP 0807667 appears to describe a similar extender comprising wholly or partially of a paraffin oil comprising 36-40 % cyclic paraffin oils and 58 to 64% non-cyclic paraffin oils. WO99/65979 describes an oil resistant sealant composition comprising a plasticiser which may include paraffinic or naphthenic oils and mixtures thereof amongst other plasticisers.

EP1481038 describes the use of a hydrocarbon fluid containing more than 60 wt.% naphthenics, at least 20 wt.% polycyclic naphthenics and an ASTM D-86 boiling point of from 235°C to 400°C. EP1252252 describes the use of an extender comprising a hydrocarbon fluid having greater than 40 parts by weight cyclic paraffinic hydrocarbons and less than 60 parts by weight monocyclic paraffinic hydrocarbons based on 100 parts by weight of hydrocarbons. EP1368426 describes a sealant composition for use with alkyd paints containing a liquid paraffinic hydrocarbon “extender” which preferably contains greater than 40% by weight of cyclic paraffins.

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[0010] It will be appreciated by the reader that there is a degree of overlap between plasticisers and extenders used for silicone polymer based compositions. This is at least partially due to the relative decrease in compatibility of the organic compounds concerned with the silicone compositions.

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[0011] Silicone rubber compositions which can, but generally do not, involve curing via a condensation reaction pathway are used for a wide variety of applications including automotive, aviation and aerospace products, baby care products such as teats for bottles, insulators for power and utilities applications, extruded profiles, gaskets and seals for e.g. air water, fuel and oil applications e.g. hoses, keypads, in medical and office equipment such as protective equipment and masks, rollers for e.g. photocopiers, sponges, and wire and cable coating applications. For such applications it is imperative that the shrinkage during curing of the composition is kept to a minimum to avoid problems with their end use i.e. in the case of cable coating one can't afford for the loss of the electrical integrity of the casing around the wire. Hence, for such applications industry practise teaches that extenders and/or plasticisers, particularly organic extenders and/or organic plasticisers are unusable because of the certainty that any significant shrinkage is detrimental to the applications typically used for the resulting cured products. One result of the above is that the cost of silicone rubber is significantly greater than organic rubber and/or natural rubber products. This cost differential results in the fact that whilst silicone rubbers provide the user with significant technical benefits, the cost of such products

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is considered prohibitive and as such industry prefers to utilise cheaper options because the lower price for organic and natural rubbers outweigh the technical benefits.

5 [0012] One of the biggest problem relating to the use of organic plasticisers and or extenders in silicone compositions is compatibility. Whilst the volatile nature of many of the unreactive plasticisers and extenders used results in shrinkage during the curing process, the actual chemical nature of the sealant composition and organic plasticiser and/or organic extender can result in significant compatibility problems
10 both during pre-cure storage and post-cure because the plasticisers and extenders are not part of the cure reaction mechanism . Typically plasticisers are more compatible with polymer compositions than extenders and tend to be significantly less volatile and as such are significantly more likely to remain at high levels within the polymer matrix after curing.

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[0013] Extenders need to be both sufficiently compatible with the remainder of the composition and as non-volatile as possible at the temperature at which the resulting cured elastomeric solid is to be maintained (e.g. room temperature).

20 [0014] Compatibility of organic extenders and/or plasticisers with the other ingredients in an organopolysiloxane based polymer composition, is a significantly greater problem than with respect to organic based polymers, silicone polymers into which the extenders and/or plasticisers are introduced tend to be highly viscous polymers, and the chemical nature of the polymer being organopolysiloxane based as
25 opposed to organic based can have significant effects on compatibility. The level of compatibility effectively determines the amount of extender and/or plasticiser which can be introduced into a polymer composition. Typically this results in the introduction of significantly lower amounts of, in particular, extenders into the composition than may be desired because the extender will not physically mix into
30 the polymer composition sufficiently well, particularly with the pre-formed polymer which is usually the largest component, other than the filler, in the composition.

[0015] US4526954 describes a polyorganosiloxane composition comprising a polyorganosiloxane having specific unsaturated groups which is blended after polymerisation with additives such as fillers, reactive or unreactive plasticisers and catalysts. EP1182231 describes a heat curable silicone elastomer composition prepared by blending two pre-prepared diorganopolysiloxane gums both containing alkenyl groups with a silica filler, a hydroxy terminated polysiloxane fluid and an organohydrogenpolysiloxane cross-linking agent a low compression set additive and an addition cure catalyst. GB1175263 describes room temperature vulcanisable compositions comprising blends of a pre-prepared curable organopolysiloxane and a curable organic polymer. Compositions optionally include fillers and plasticisers. US5641831 describes a method for the production of a silicone rubber article prepared by blending a pre-prepared silicone polymer, at least one cross-linkable process fluid and low pressure and high pressure peroxide catalysts for use in a two stage vulcanisation process. The process fluid has a viscosity of 5 to 100 cSt a hydroxy content of 2 to 20 %by weight and a mole vinyl content of 0.2 to 13 %.

[0016] The applicants have now identified a means of avoiding many of the post-cure compatibility and shrinkage problems currently connected with the use of extended and/or plasticised organopolysiloxane compositions thereby enabling the use of such extenders and plasticisers not only in silicone sealant formulations but also in silicone rubber formulations.

[0017] A method for the production of an extended and/or plasticised organopolysiloxane composition comprising the steps:-

- Mixing a polysiloxane containing polymer and/or precursors thereof
- with
- an extender and/or plasticiser prior to or during polymerisation of the polysiloxane containing polymer and/or
- a filler prior to and/or during polymerisation and, if required
- introducing residual extender and/or plasticiser and/or filler together with a first cure package for curing the polymer subsequent to polymerisation

- characterised in that the extender and/or plasticiser is chemically functionalised so as to substantially not participate in any chemical reaction(s) with the polymer and/or its precursors but is chemically attached to the cross-linked matrix of the resulting cured elastomer during curing.

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[0018] Hence as a consequence of the above the filler and/or extender/plasticiser may be mixed with the polymer and/or its precursors prior to and/or during the polymer polymerisation process, by making a pre-blend of polymer and extender/plasticiser before introducing the other ingredients of the composition or
10 merely as a ingredient in the composition. Preferably the plasticiser/extender is always introduced into the mixture before or simultaneously with the filler, more preferably before the filler. Most preferably the plasticiser/extender is introduced prior to or during the polymerisation of the polymer.

15 [0019] A method for the production of a cured organopolysiloxane based elastomer comprising the steps of

(i) Preparing an extended and/or plasticised polysiloxane containing polymer by intermixing the polymer and/or precursors thereof with
20 an extender and/or plasticiser and optionally filler, prior to or during polymerisation of the polysiloxane containing polymer

(ii) Mixing the resulting extended and/or plasticised polysiloxane containing polymer product with: a suitable cure system to form a
25 curable composition; and optionally residual extender and/or filler; and

(iii) curing the resulting polymer composition to form a cured elastomer having a cross-linked matrix; characterised in that the extender and/or plasticiser is chemically functionalised so as to substantially
30 not participate in any chemical reaction(s) with the polymer and/or

its precursors during steps (i) or (ii) but is chemically attached to the cross-linked matrix of the resulting cured elastomer during curing.

5 [0020] A method for the production of an extended and/or plasticised organopolysiloxane composition comprising the steps:-

10 (i) Preparing an extended and/or plasticised polysiloxane containing polymer by intermixing the polymer and/or precursors thereof with an extender and/or plasticiser and optionally filler, prior to or during polymerisation of the polysiloxane containing polymer

15 (ii) Mixing the resulting polysiloxane containing polymer product with: a suitable first cure system and optionally residual extender and/or filler to form a curable composition; characterised in that the extender and/or plasticiser is chemically functionalised so as to substantially not participate in any chemical reaction(s) with the polymer and/or its precursors during step (i) or step (ii) but is chemically attached to the cross-linked matrix of the resulting cured elastomer during curing.

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[0021] Preferably the plasticiser and/or extender participates in the cure process and forms an integral part of the cross-linked matrix of the resulting cured elastomer.

25 [0022] The concept of “comprising” where used herein is used in its widest sense to mean and to encompass the notions of “include” and “consist of”. All viscosity measurements referred to herein were measured at 25°C unless otherwise indicated.

30 [0023] Preferably the extended and/or plasticised polysiloxane containing polymer is prepared by polymerising siloxane containing monomers and/or oligomers in the presence of

the extender and/or plasticiser,
a suitable catalyst and

optionally an end-blocking agent; and

Where required quenching the polymerisation process;

5 [0024] For the sake of clarification, the term “oligomer” and derivatives thereof are used herein to mean monomer(s) or oligomer(s) or polymer(s) utilised as a starting material involved in a polymerisation process.

10 [0025] Preferably each extender and or plasticiser is miscible or at least substantially miscible with the monomeric/oligomeric starting materials with which they are initially mixed, and more particularly with both intermediate polymerisation reaction products and the final polymerisation product. Extenders and/or plasticisers which are “substantially miscible” are intended to include extenders and/or plasticisers which are completely or largely miscible with the monomer(s) and/or the reaction mixture during polymerisation and hence may include low melting point
15 solids which become miscible liquids in a reaction mixture during the polymerisation process.

[0026] Any appropriate polymerisation process may be utilised to generate the polymer in (i) in the presence of the extender and/or plasticiser provided that the
20 polymer, polymer intermediates and monomers and/or oligomers substantially do not chemically react and preferably do not react with the extender(s) and/or plasticiser(s).

[0027] Preferred polymerisation processes where the polymer is prepared in the presence of the extender and/or plasticiser, which may be utilised in accordance with
25 this invention include polycondensation, polyaddition and chain extension polymerisation routes:-

POLYCONDENSATION ROUTE

30 [0028] One preferred polymerisation process is polycondensation using extenders and/or plasticisers which do not become chemically involved in the polymerisation reaction.

[0029] Polycondensation (otherwise known as condensation polymerisation) is the polymerisation of monomers and/or oligomers with the elimination of low molecular weight by-product(s) such as water, ammonia or methanol etc.). In this embodiment preferably each monomer/oligomer comprise at least two condensable groups preferably terminal groups, that will, in appropriate conditions, undergo a condensation reaction. Preferably the condensable groups in the present invention are hydroxyl containing terminal groups or hydrolysable end groups (e.g. alkoxy groups).

[0030] An organosiloxane containing polymer is intended to mean a polymer comprising multiple organopolysiloxane groups per molecule and is intended to include a polymer substantially containing only organopolysiloxane groups in the polymer chain or polymers where the backbone contains both organopolysiloxane groups and e.g. organic polymeric groups in chain.

[0031] Polycondensation type polymerisation reactions are most generally linked to the interaction of compounds having hydroxyl and/or hydrolysable end groups such as alkoxy groups, which can interact with the release of e.g. water or methanol or the like.

[0032] A selection of condensation reactions which may be alternatively utilised for the polymerisation process in accordance with this embodiment of the invention between monomers and/or oligomers in accordance with the present invention include:-

- 1) the condensation of organohalosilyl groups with an organoalkoxysilyl groups
- 2) the condensation of organohalosilyl groups with organoacyloxysilyl groups
- 3) the condensation of organohalosilyl groups with organosilanols
- 4) the condensation of organohalosilyl groups with silanolates
- 5) the condensation of organo-hydrosilyl groups with organosilanol groups
- 6) the condensation of organoalkoxysilyl groups with organoacyloxysilyl groups
- 7) the condensation of organoalkoxysilyl groups with organosilanol groups
- 8) the condensation of organoaminosilyl groups with organosilanols

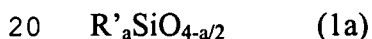
- 9) the condensation of organoacyloxysilyl groups silanolate groups
- 10) the condensation of organoacyloxysilyl groups with organosilanols
- 11) the condensation of organooximosilyl groups with organosilanol groups
- 12) the condensation of organoenoxysilyl groups with organosilanols
- 5 13) The condensation of a siloxane compound comprising one or more hydrosilane functional groups with a siloxane compounds containing at least one alkoxysilane functional group, generating hydrocarbon by-products.

[0033] Any of the above condensation type reactions may be used for the block co-
 10 polymerisation of monomer(s)/oligomer(s) and as such may be the basis for the polymerisation process in accordance with the present invention.

[0034] Preferably the condensable end groups are hydroxyl end groups or hydrolysable end groups, most preferably alkoxy groups.

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[0035] Hence, one preferred method for the polymerisation process is the polymerisation of straight chain and/or branched organopolysiloxanes with condensable end groups comprising units of formula (1a)



wherein each R' may be the same or different and denotes a hydrocarbon group having from 1 to 18 carbon atoms, a substituted hydrocarbon group having from 1 to 18 carbon atoms or a hydrocarbonoxy group having up to 18 carbon atoms and $\underline{a}$ has,
 25 on average, a value of from 1 to 3, preferably 1.8 to 2.2.

[0036] For the purpose of this application in the case of hydrocarbon groups "Substituted" means one or more hydrogen atoms in the hydrocarbon group has been replaced with another substituent. Examples of such substituents include, but are not
 30 limited to, halogen atoms such as chlorine, fluorine, bromine, and iodine; halogen atom containing groups such as chloromethyl, perfluorobutyl, trifluoroethyl, and nonafluorohexyl; oxygen atoms; oxygen atom containing groups such as

(meth)acrylic and carboxyl; nitrogen atoms; nitrogen atom containing groups such as amines, amino-functional groups, amido-functional groups, and cyano-functional groups; sulphur atoms; and sulphur atom containing groups such as mercapto groups.

5 **[0037]** The hydrocarbon groups of R' may be of any suitable type but are preferably alkyl groups and optionally to an extent unsaturated groups such as alkenyl groups and alkynyl groups. The presence of unsaturated groups in the side chains means that the condensable groups used in the polymerisation process do not require end-capping before they are mixed into the composition to be cured because the unsaturated
10 groups situated along the polymer chain may be utilised in a hydrosilylation cure or peroxide cure process for curing the polymer composition subsequently prepared. Particularly preferred examples of groups R' include methyl, ethyl, propyl, butyl, vinyl, hexenyl, cyclohexyl, phenyl, tolyl group, a propyl group substituted with chlorine or fluorine such as 3,3,3-trifluoropropyl, chlorophenyl, beta-
15 (perfluorobutyl)ethyl or chlorocyclohexyl group. Preferably, at least some and more preferably substantially all of the groups R' are methyl. When no unsaturated groups, particularly alkenyl and/or alkynyl groups are present per molecule of polymer, some R' groups may be hydrogen groups.

20 **[0038]** Preferably the polydiorganosiloxane monomer/oligomer starting materials are polydialkylsiloxanes, most preferably polydimethylsiloxanes. They are preferably substantially linear materials, which have siloxane end groups of the formula $R''_3SiO_{1/2}$, wherein each R'' is the same or different and is R' or a condensable group. Any suitable combination of condensable end groups may be used for the
25 polymerisation process of the present invention (i.e. the condensable groups chosen must be able to undergo a condensation reaction together in order to polymerise). Preferably at least one R'' group per molecule is a hydroxyl or hydrolysable group. Typically the condensable groups used as monomer/oligomer end-groups are preferably silicon-bonded hydroxyl groups or hydrolysable groups such as alkoxy
30 groups, which may form silanol groups in situ or the like but may be any groups which will participate in a polycondensation of the monomer/oligomer in the presence

of the diluent in accordance with the present invention. In a small amount (<20%) of the $R''_3SiO_{1/2}$ groups, each R'' group may be an alkyl group.

[0039] Preferably the starting materials have a viscosity of between 10mPa.s and 50000mPa.s at 25°C. Some of the starting materials may comprise non-hydrolysable end-groups but this is not desired. It will also be appreciated that where required organic monomers and/or oligomers having appropriate condensable end groups so as to be polymerisable with said organopolysiloxane monomers and/or oligomers may be introduced in order to form ABA or AB_n type block copolymers.

[0040] In the case of polydiorganosiloxane co-polymers the polymeric chain may comprise blocks made from chains of units depicted in figure (1a) where a is 2 and the two R' groups are:-

both alkyl groups (preferably both methyl or ethyl), or
alkyl and phenyl groups, or
alkyl and fluoropropyl, or
alkyl and vinyl or
alkyl and hydrogen groups.

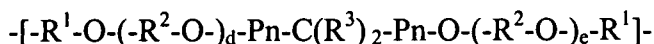
Typically at least one block will comprise siloxane units in which both R' groups are alkyl groups.

[0041] In accordance with the present invention organic monomers and/or oligomers may be utilised with the intention of providing block copolymers with the siloxane containing monomers and/or oligomers. Preferably the organic monomers and/or oligomers comprise two or more condensable groups which are condensable with the condensable groups of the siloxane monomers and/or oligomers. Examples of organic monomers which may be used, providing they have a suitable number of condensable groups attached thereto, in accordance with the present invention include, for example polystyrene and/or substituted polystyrenes such as poly(α -methylstyrene), poly(vinylmethylstyrene), poly(p -trimethylsilylstyrene) and poly(p -trimethylsilyl- α -methylstyrene). Other organic components may include acetylene terminated

oligophenylenes, vinylbenzyl terminated aromatic polysulphones oligomers, aromatic polyesters and aromatic polyester based monomers.

[0042] However perhaps the most preferred organic based oligomers are polyoxyalkylene based oligomers having two or more condensable groups per molecule. Such polyoxyalkylene compounds preferably comprise a linear predominantly oxyalkylene polymer comprised of recurring oxyalkylene units illustrated by the average formula $(-C_bH_{2b}-O-)_c$ wherein b is an integer from 2 to 4 inclusive and c is an integer of at least four. The average molecular weight of each polyoxyalkylene polymer block may range from about 50 to about 10,000. Moreover, the oxyalkylene units are not necessarily identical throughout the polyoxyalkylene monomer, but can differ from unit to unit. A polyoxyalkylene block, for example, can be comprised of oxyethylene units, $(-C_2H_4-O-)$; oxypropylene units $(-C_3H_6-O-)$; or oxybutylene units $(-C_4H_8-O-)$; or mixtures thereof.

[0043] Other polyoxyalkylene monomers and/or oligomers having two or more condensable groups per molecule may include for example units of the structure-



in which Pn is a 1,4-phenylene group, each R^1 is the same or different and is a divalent hydrocarbon group having 2 to 8 carbon atoms, each R^2 is the same or different and, is, an ethylene group, propylene group, or isopropylene group, each R^3 is the same or different and is a hydrogen atom or methyl group and each of the subscripts d and e is a positive integer in the range from 3 to 30.

[0044] The polycondensation process as hereinbefore described requires a suitable condensation catalyst for reactions to proceed. Any suitable polycondensation catalyst may be utilised. These include protic acids, Lewis acids, organic and inorganic bases, metal salts and organometallic complexes. Lewis acid catalysts. (a "Lewis acid" is any substance that will take up an electron pair to form a covalent bond).suitable for the polymerisation in the present invention include, for example,

boron trifluoride FeCl_3 , AlCl_3 , ZnCl_2 , ZnBr_2 , catalysts of formula $\text{M}^1\text{R}^4_f\text{X}^1_g$ where M^1 is B, Al, Ga, In or Tl each R^4 is independently the same (identical) or different and represents a monovalent aromatic hydrocarbon radical having from 6 to 14 carbon atoms, such monovalent aromatic hydrocarbon radicals preferably having at least one
 5 electron-withdrawing element or group such as $-\text{CF}_3$, $-\text{NO}_2$ or $-\text{CN}$, or substituted with at least two halogen atoms; X^1 is a halogen atom; f is 1, 2, or 3; and g is 0, 1 or 2; with the proviso that $f+g=3$. One example of such a catalyst being $\text{B}(\text{C}_6\text{F}_5)_3$.

[0045] Catalysts which will promote condensation reactions but also act as
 10 equilibration catalysts such as sulphuric acid, hydrochloric acid, Lewis acids, sodium hydroxide, tetramethylammonium hydroxide, tetrabutyl phosphonium silanolate and amines may be used but are not preferred provided the presence of low molecular weight species in the polymer is not to be avoided, or provided the catalyst is inactivated prior to the rearrangement of polymers.

15 [0046] Further suitable condensation catalysts which may be used as the catalyst for the polymerisation reaction in the present invention include condensation catalysts incorporating tin, lead, antimony, iron, cadmium, barium, manganese, zinc, chromium, cobalt, nickel, aluminium, gallium or germanium and zirconium.
 20 Examples include metal triflates, organic tin metal catalysts such as triethyltin tartrate, tin octoate, tin oleate, tin naphthate, butyltintri-2-ethylhexoate, tinbutyrate, carbomethoxyphenyl tin trisuberate, isobutyltintriceroate, and diorganotin salts especially diorganotin dicarboxylate compounds such as dibutyltin dilaurate, dimethyltin dibutyrate, dibutyltin dimethoxide, dibutyltin diacetate, dimethyltin
 25 bisneodecanoate Dibutyltin dibenzoate, , stannous octoate, dimethyltin dineodeconoate, dibutyltin dioctoate of which dibutyltin dilaurate, dibutyltin diacetate are particularly preferred.

[0047] Titanate and/or zirconate based catalysts may comprise a compound
 30 according to the general formula $\text{Ti}[\text{OR}^5]_4$ and $\text{Zr}[\text{OR}^5]_4$ respectively where each R^5 may be the same or different and represents a monovalent, primary, secondary or tertiary aliphatic hydrocarbon group which may be linear or branched containing from

1 to 10 carbon atoms. Optionally the titanate may contain partially unsaturated groups. However, preferred examples of R^5 include but are not restricted to methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl and a branched secondary alkyl group such as 2,4-dimethyl-3-pentyl. Preferably, when each R^5 is the same, R^5 is an
 5 isopropyl, branched secondary alkyl group or a tertiary alkyl group, in particular, tertiary butyl.

[0048] Alternatively, the titanate may be chelated. The chelation may be with any suitable chelating agent such as an alkyl acetylacetonate such as methyl or
 10 ethylacetylacetonate. Any suitable chelated titanates or zirconates may be utilised. Preferably the chelate group used is a monoketoester such as acetylacetonate and alkylacetoacetate giving chelated titanates such as, for example diisopropyl bis(acetylacetonyl)titanate, diisopropyl bis(ethylacetoacetonyl)titanate, diisopropoxytitanium Bis(Ethylacetoacetate) and the like. Examples of suitable
 15 catalysts are additionally described in EP1254192 and WO200149774 which are incorporated herein by reference.

[0049] More preferred are condensation specific catalysts. These include acidic condensation catalysts of the formula R^6SO_3H in which R^6 represents an alkyl group
 20 preferably having from 6 to 18 carbon atoms such as for example a hexyl or dodecyl group, an aryl group such as a phenyl group or an alkaryl group such as dinonyl- or didoecyl-naphthyl. Water may optionally be added. Preferably R^6 is an alkaryl group having an alkyl group having from 6 to 18 carbon atoms such as dodecylbenzenesulphonic acid (DBSA). Other condensation specific catalysts include n-
 25 hexylamine, tetramethylguanidine, carboxylates of rubidium or caesium, hydroxides of magnesium, calcium or strontium and other catalysts as are mentioned in the art, e.g. in GB895091, GB918823 and EP 0382365. Also preferred are catalysts based on phosphonitrile chloride, for example those prepared according to US 3839388, US4564693 or EP215470 and phosphonitrile halide ion based catalysts, as described
 30 in GB2252975, having the general formula $[X^2(PX^2_2=N)_hPX^2_3]^+[M^2X^2_{(j-k+1)}R^{III}_k]^-$, wherein X^2 denotes a halogen atom, M^2 is an element having an electronegativity of from 1.0 to 2.0 according to Pauling's scale, R^{III} is an alkyl group having up to 12

carbon atoms, h has a value of from 1 to 6, j is the valence or oxidation state of M^2 and k has a value of from 0 to $v-1$.

[0050] Alternatively, the catalyst may comprise an oxygen-containing
 5 chlorophosphazene containing organosilicon radicals having the following general formula:-



10 in which

Z^1 represents an organosilicon radical bonded to phosphorus via oxygen, a chlorine atom or the hydroxyl group and m represents 0 or an integer from 1 to 8. The catalyst may also comprise condensation products of the above and/or tautomers thereof (the catalyst exists in a tautomeric form when Z^1 is a hydroxyl group). All or some of the
 15 chlorine atoms can be replaced by radicals Q , in which Q represents the hydroxyl group, monovalent organic radicals, such as alkoxy radicals or aryloxy radicals, halogen atoms other than chlorine, organosilicon radicals and phosphorus-containing radicals. The oxygen-containing chlorophosphazenes are preferably those in which no chlorine atom is replaced by a radical Q .

20

[0051] A further alternative catalyst which might be used as the catalyst in the present invention is any suitable compound providing a source of anions comprising at least one quadri-substituted boron atom and protons capable of interaction with at least one silanol group as defined in WO 01/79330. For this type of catalyst, it is
 25 important that the boron containing anion does not itself form a covalent bond directly to a silicon atom and that it does not decompose or rearrange to produce an anion which forms a covalent bond directly to a silicon atom. Suitable materials include those incorporating one or more boron atoms disposed within a grouping and several, for example ten or more, halogen atoms connected with each boron atom.
 30 The halogen atoms in such compound may be connected to boron atoms by linkages incorporating at least one carbon atom and are selected from fluorine, chlorine and bromine, the most preferred being fluorine.

[0052] Preferred anions incorporate one or more atoms of boron having four organic substituents thereon the most preferred being quadri-substituted borates. The organic substituents are suitably halogenated hydrocarbon groups. Such as pentafluorinated phenyl groups and bis (trifluoromethyl) phenyl groups and preferred materials have four such groups bonded to each boron atom. Examples include tetrakis (pentafluorophenyl) borate anion (perfluorinated aryl borate ion) and the material is preferably employed as the acid of this anion namely $H^+ \{(C_6F_5)_4B\}^-$. Other operative materials include anions having two quadri-substituted boron atoms, for example diperfluorinatedaryl borate ions, e.g. $H^+ \{B(C_6F_5)_3CNB(C_6F_5)_3\}^-$. Other suitable boron-containing anions for use in the process of the present invention include carboranes, for example of the formula $\{CB_9H_{10}\}^-$, $\{CB_9X^2_5H_5\}^-$, $\{CB_{11}H_{12}\}^-$ and $\{CB_{11}X^2_6H_6\}^-$ wherein each X^2 is the same or different and is as hereinbefore described. Carboranes may contain boron atoms which are more highly substituted than quadri-substituted, e. g. pentasubstituted and hexa-substituted, and for the sake of clarity "quadri-substituted" where used herein is intended to include those anions containing quadri-substituted and higher substituted boron atoms.

[0053] A further group of catalysts which may be utilised are materials providing in the polymerisation reaction mixture a source of (a) protons capable of interaction with at least one of said silicon bonded hydroxy or alkoxy groups and (b) weakly coordinating anions (i.e. an anion which has a negative charge distributed through a comparatively large radical in such a way that the anion is comparatively weakly attractive to proton in the organosilicon reaction mixture i.e. e. is not a strong nucleophile). These include materials having one or more suitable atoms M^2 , of an element selected from the group consisting of boron, niobium, and aluminium, disposed within the grouping and several, for example ten or more, halogen atoms connected with each atom M^2 . The halogen atoms in such compound may be connected to atoms M^2 by linkages incorporating at least one carbon atom. The halogen atoms are preferably selected from fluorine, chlorine and bromine, the most preferred being fluorine. The preferred weakly coordinating anions may incorporate one or more atoms M of any suitable element capable of supporting an anion

substituted to the extent of one more substituent on the atom M^2 than its neutral valence, for example four substituents on aluminium or boron or six substituents on niobium. Preferred anions incorporate one or more atoms of boron having four organic substituents thereon the most preferred being quadri-substituted borates. The organic substituents are suitably hydrocarbon groups. Three and preferably four of these hydrocarbon groups are preferably aromatic groups, and are preferably highly halogenated. Preferred halogenated hydrocarbons are pentafluorinated phenyl groups and bis (trifluoromethyl) phenyl groups and preferred materials have four such groups bonded to each boron atom. One operative weakly co-ordinating anion is the tetrakis (pentafluoro phenyl) borate anion (otherwise herein referred to as the perfluorinated aryl borate ion) and the material providing the source of protons (a) and weakly co-ordinating anions (b) is the acid of this anion namely $H^+ \{(C_6F_5)_4B\}^-$.

[0054] The temperatures and pressures used in the process can be the same as those in the processes known to date for the polycondensation of organosilicon compounds.

[0055] The polymerization reaction with the present invention may be carried out at any appropriate temperature and pressure in either batch or continuous mode. The reaction conditions need to be set depending on the specific catalyst used and the chemical equilibrium of the polymerization reaction. In the case of the phosphazene catalysed methods the polymerisation may occur at temperatures of from room temperature to 200°C preferably between 50°C to 200°C, more preferably 80°C to 160°C.

[0056] The activity of the catalyst is preferably quenched by using a neutralizing agent which reacts with the catalyst to render it non-active. Typically in the case of the acid type condensation catalysts the neutralising agent is a suitable base, for example, an amine such as a mono/di and trialkanolamine, specific examples include but are not limited to monoethanolamine (MEA) and triethanolamine (TEA), magnesium oxide and/or calcium carbonate. In the case of systems using a DBSA catalyst alternative quenching means include aluminasilicate zeolite materials that were found to absorb DBSA and leave a stable polymer. In most cases catalyst residues remain in the

polymer product or where appropriate may be removed by filtration or alternative methods. In the case of phosphazene based catalysts once the desired polymer viscosity has been reached, the viscosity of the organosilicon compound obtained in the process can be kept substantially constant by a procedure in which the catalyst used, or a reaction product which has been formed incorporating catalyst residues which likewise promotes the polymerisation process, is inhibited or deactivated by addition of inhibitors or deactivators. Any suitable inhibitors and/or inactivators may be used. Specific examples include but are not restricted to triisnonylamine, n-butyllithium, lithium siloxanolate, hexamethylcyclotrisilazane and hexamethyldisilazane.

[0057] Any suitable method for making the polymer in accordance with the method of the present invention may be used.

[0058] The polycondensation reactions may be carried out at any suitable pressure although in order to facilitate removal of by-products formed during the condensation, for example, water, HCl or alcohol, the polymerisation process may take place at a pressure below 80 kPa. Condensation type reactions involving equilibration, may be carried out at pressures above atmospheric if so desired.

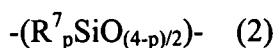
[0059] The polymerisation process in accordance with the invention may be carried out either batchwise or continuously using any suitable mixers. Where the polycondensation by-product is water, the water can either be removed by chemical drying using e.g. hydrolysable silanes like methyltrimethoxysilane or by physical separation using evaporation, coalescing or centrifuging techniques.

[0060] Hence, in this embodiment of the invention preferably the resulting polymer used in the present invention is a polysiloxane containing polymer containing at least two OH or otherwise condensable terminal groups. Hence, the polymer has the general formula



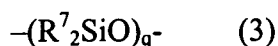
X and X³ are independently selected from siloxane groups which terminate in hydroxyl or hydrolysable groups and A is a siloxane containing polymeric chain.

[0061] It will be appreciated that A will be dependent on the structure of the monomers and oligomers used as starting materials (as described above) and the reaction pathway of polymerisation. Any combination of the monomer/oligomers described above may be utilised as the basis of A in the prepared polymer. Hence, examples of typical siloxane groups A in formula (I) are those which comprise a polydiorganosiloxane chain. Thus group A preferably includes siloxane units of formula (2)



in which each R⁷ is independently an organic group such as a hydrocarbon group having from 1 to 18 carbon atoms, a substituted hydrocarbon group having from 1 to 18 carbon atoms or a hydrocarbonoxy group having up to 18 carbon atoms and p has, on average, a value of from 1 to 3, preferably 1.8 to 2.2. Preferably R⁷ is a hydrocarbyl group having from 1 to 10 carbon atoms optionally substituted with one or more halogen group such as chlorine or fluorine and p is 0, 1 or 2. Particular examples of groups R⁷ include methyl, ethyl, propyl, butyl, vinyl, hexenyl, 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. Suitably, at least some and preferably substantially all of the groups R⁷ are methyl.

[0062] Group A in the compound of formula (1) may include any suitable siloxane or siloxane/organic molecular chain providing the resulting polymer a viscosity (in the absence of diluents in accordance with the present invention of up to 20 000 000 mPa.s, at 25°C (i.e. up to or even more than 200 000 units of formula (2)). In one preferred embodiment A is a linear organopolysiloxane molecular chain (i.e. p = 2) for all chain units. Preferred materials have polydiorganosiloxane chains of units according to the general formula (3)



in which each R^7 is as defined above and is preferably a methyl group and q has a value of up to at least (or even more than) 200 000. Suitable polymers have viscosities of up to 20 000 000mPa.s at 25°C. In one preferred alternative the extended and/or plasticised polysiloxane containing polymer comprises hydrolysable end groups and pendant unsaturated groups such that polymerisation takes place via a condensation process and cure is carried out with a hydrosilylation process.

[0063] As previously indicated if organic monomers/oligomers are utilised as starting materials in the polymerisation process of the present invention A may be a block copolymeric backbone comprising at least one block of siloxane groups of the type depicted in formula (2) above and an organic component comprising any suitable organic based polymer backbone for example the organic polymer backbone prepared by the introduction of aforementioned organic monomers/oligomers into the polymer backbone.

[0064] X and X^3 are independently selected from siloxane groups which terminate in hydroxyl or hydrolysable groups. Examples of hydroxyl-terminating or hydrolysable groups which terminate X or X^3 include $-\text{Si}(\text{OH})_3$, $(\text{R}^a)\text{Si}(\text{OH})_2$, $-(\text{R}^a)_2\text{SiOH}$, $-\text{R}^a\text{Si}(\text{OR}^b)_2$, $-\text{Si}(\text{OR}^b)_3$, $-\text{R}^a_2\text{SiOR}^b$ or $-\text{R}^a_2\text{Si}-\text{R}^c-\text{SiR}^d_n(\text{OR}^b)_{3-n}$ where each R^a independently represents a monovalent hydrocarbyl group, for example, an alkyl group, in particular having from 1 to 8 carbon atoms, (and is preferably methyl); each R^b and R^d group is independently an alkyl or alkoxy group in which the alkyl groups suitably have up to 6 carbon atoms; R^c is a divalent hydrocarbon group which may be interrupted by one or more siloxane spacers having up to six silicon atoms; and n has the value 0, 1 or 2. Preferably X and/or X^3 contain hydroxyl groups or groups which are otherwise hydrolysable in the presence of moisture.

[0065] However, in the present embodiment of the invention where required an end-blocking compound may be additionally introduced into the polymerisation process to regulate the molecular weight of the polymer and/or add functionality. End-blocking agents are a means of controlling the reactivity /polymer chain length of the polymer by introducing compounds which will react with only one hydrolysable end group,

subsequently preventing further polycondensation. It is also a means of introducing alternative end groups on the polymer, e.g. silicon bonded hydrogen groups or alkenyl groups which may then be utilised to produce alternative reactive end groups or provide a non-reactive end group.

5

[0066] In this embodiment preferably each end-blocking compound comprises a condensable group for reaction with the end-groups of the polymer and a group which will readily chemically react when the composition is cured with components of the cure package and/or the extender and/or plasticiser(s). Hence preferably each end-blocking
10 compound comprises at least one unsaturated group preferably an alkenyl group having from 2 to 10 carbon atoms or an alkynyl group having from 2 to 10 carbon atoms. Suitable end-blocking compounds include dialkylalkenylalkoxy silane or a dialkylalkenylsilanol. Examples of such silanes are dimethyl vinylmethoxysilane, methyl vinyl dimethoxysilane, methyl phenyl vinyl ethoxysilane and in the case
15 where alkenyl end groups are required suitable end-blocking compounds include, for example alkenyl silazanes.

[0067] Preferably the resulting polymer used in the present invention is a polysiloxane containing polymer which has been end-blocked such that each polymer
20 molecule comprises at least two unsaturated groups per molecule. Whilst these unsaturated groups may be terminal groups this is not essential.

[0068] Hence, in this embodiment of the invention preferably the resulting polymer used in the present invention is a polysiloxane containing polymer containing at least
25 two unsaturated groups per molecule, Whilst these unsaturated groups may be terminal groups this is not essential.

[0069] In the case where the polymer has been end-blocked with compounds containing unsaturated groups X and X³ preferably both comprise a group which will
30 undergo an addition type reaction with a suitable cross-linking molecule or undergo a cure reaction with an organic peroxide. Preferably the addition type reaction is a hydrosilylation reaction and X and X³ contain unsaturated organic groups containing

from 2 to 10, preferably 2 to 6 carbon atoms such as alkenyl groups, alkynyl groups, acrylate groups and /or alkylacrylate groups. However, alkenyl groups are preferred. Representative, non- limiting examples of the alkenyl groups are shown by the following structures; $\text{H}_2\text{C}=\text{CH}-$, $\text{H}_2\text{C}=\text{CHCH}_2-$, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2-$,
 5 $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2-$, $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}_2-$, and $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$. Representative, non- limiting examples of alkynyl groups are shown by the following structures; $\text{HC}\equiv\text{C}-$, $\text{HC}\equiv\text{CCH}_2-$, $\text{HC}\equiv\text{CC}(\text{CH}_3)-$, $\text{HC}\equiv\text{CC}(\text{CH}_3)_2-$, $\text{HC}\equiv\text{CC}(\text{CH}_3)_2\text{CH}_2-$.

10 **[0070]** Most preferably in this embodiment X and X³ are alkenyl groups with vinyl groups being particularly preferred. A small proportion (<20%) of X groups may comprise trialkylsilyl groups, in which each alkyl group is preferably methyl or ethyl.

POLYADDITION POLYMERISATION PROCESS

15

[0071] In an alternative embodiment of the present invention the polymer may be prepared using a polyaddition copolymerisation route by reacting a siloxane containing material with:-

- i) one organopolysiloxane polymer(s) and/or
- 20 ii) one or more organic oligomer(s)

via an addition reaction pathway in the presence of an extender and/or plasticiser, a suitable catalyst and optionally an end-blocking agent; and where required quenching the polymerisation process;

25

[0072] An “addition polymerisation” process is a polymerisation process whereby unlike in a condensation reaction no by-products such as water or alcohols are generated from the monomer co-reactants during polymerisation. A preferred addition polymerisation route is a hydrosilylation reaction between an unsaturated
 30 organic group e.g. an alkenyl or alkynyl group and an Si-H group in the presence of a suitable catalyst.

[0073] The siloxane containing material is preferably an organopolysiloxane monomer or oligomer which contains groups capable of undergoing addition type reactions with polymer (i) and/or oligomer (ii). The preferred addition reaction involved in the addition copolymerisation in accordance with the present invention is a hydrosilylation reaction
 5 between an unsaturated group and an Si-H group but any other suitable addition type reaction may be involved.

[0074] The link between the siloxane containing material and organopolysiloxane polymer (a) or organic oligomer(b) may comprise, for the sake of example any one of
 10 the following divalent organic groups:-

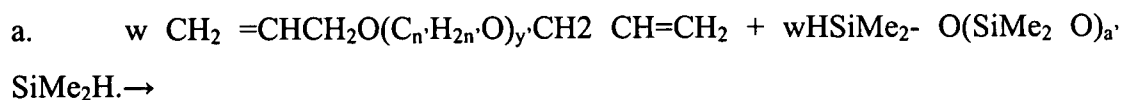
--R⁸ --
 --R⁸--CO--
 --R⁸--NHCO--
 15 --R⁸--NHCONH—R⁹--NHCO--
 --R⁸--OOCNH—R⁹--NHCO--

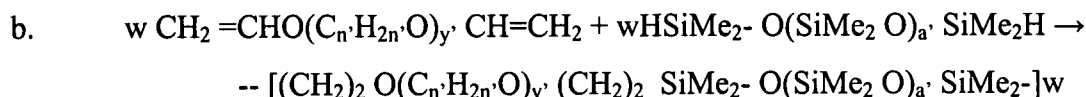
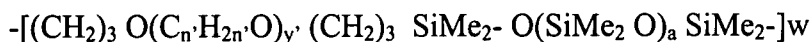
and the like, wherein R⁸ is a divalent alkylene radical such as ethylene, propylene, butylene and the like; and R⁹ represents a divalent alkylene group, e.g. R⁸, or a
 20 divalent arylene group, such as a phenylene radical, i.e. —C₆H₄--. Illustrative of the other preferred examples of said divalent organic groups are; --(CH₂)₂ CO--; --(CH₂)₃ NHCO--; --(CH₂)₃ NHCONH—C₆H₄--NHCO--; --(CH₂)₃ OOCNH—C₆H₄--NHCO--; and the like. Most preferably as the addition copolymerisation reaction preferred is a hydrosilylation reaction the link is in the form of a divalent alkylene group.

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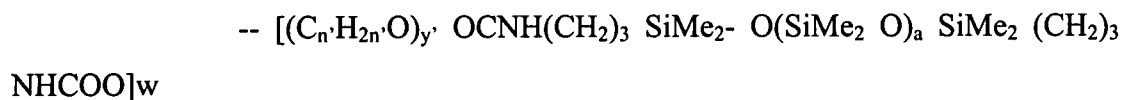
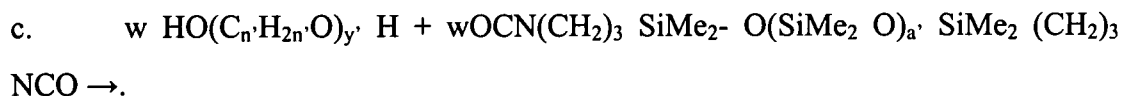
[0075] The nature of the reactive groups involved in the copolymerisation reaction determines the structure of the divalent organic group linking the constituents of the polymerisation reaction. Typically the reactions involved in the polymerisation of copolymers in accordance with the present invention may be as follows:-

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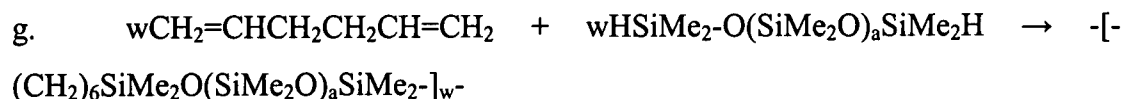
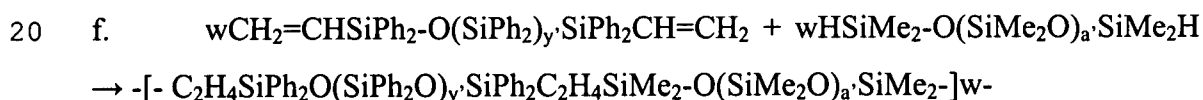
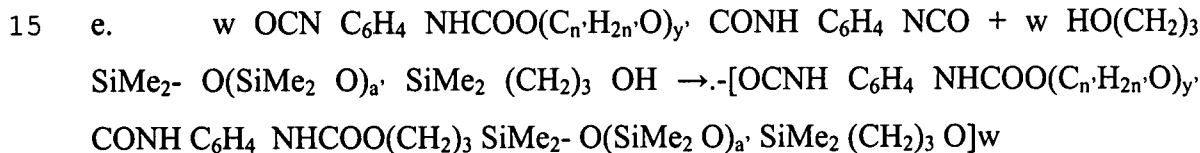
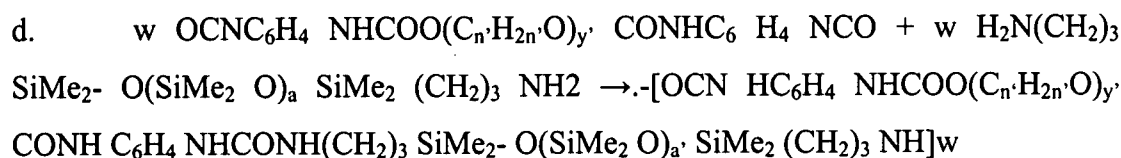




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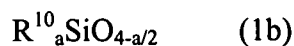


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wherein Me represents a methyl radical; n' is an integer of from 2 to 4 inclusive; a' is an integer of at least 5; y' is an integer of at least 4 and w is an integer of at least 4.

[0076] Whilst the siloxane containing material may comprise any of the groups in reactions (a) to (g) above, it is preferably an organopolysiloxane monomer, more preferably in the form of a straight chain and/or branched organopolysiloxane comprising units of formula (1a)

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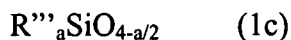
wherein each R^{10} may be the same or different and is R' is as hereinbefore described
 5 or hydrogen and a is as hereinbefore described. When the siloxane containing material is an Organopolysiloxane monomer, said organopolysiloxane monomer must have at least one group which is reactable with at least two groups, typically the terminal groups, of polymer (i) and/or oligomer (ii) via an addition reaction process. Preferably when the siloxane containing material is an organopolysiloxane monomer said
 10 organopolysiloxane monomer comprises at least one Si-H per molecule, preferably at least two Si-H groups per molecule. Preferably when the siloxane containing material is an organopolysiloxane said organopolysiloxane is end-blocked with a silyl group of the formula $H(alkyl)_2Si-$, and each alkyl group may be the same or different and is preferably methyl or ethyl. Preferably when the siloxane containing material is an
 15 organopolysiloxane said organopolysiloxane has a viscosity of between 10mPa.s and 5000mPa.s at 25°C

[0077] In cases where the siloxane containing material comprises only one addition reactable group and polymer (i) and/or oligomer (ii) comprises two addition reactable
 20 groups which will react with the siloxane containing material, the resulting product will be an "ABA" type polymeric product. Whereas when both the siloxane containing material comprises two addition reactable groups and polymer (a) and/or oligomer (b) comprises two addition reactable groups which will react with the siloxane containing material interaction between the two components would lead to
 25 (AB) n block copolymers in which the length of the polymer is largely determined by the relative amounts of the two constituents.

[0078] Organopolysiloxane polymer (i) may comprise any suitable organopolysiloxane polymeric backbone but is preferably linear or branched, and comprises at least one,
 30 preferably at least two substituent groups which will react with the aforementioned groups in the siloxane containing material via an addition reaction pathway., Preferably the or each substituent group of polymer (i) is a terminal group. When the siloxane

containing material comprises at least one Si-H group, the preferred substituent groups on organopolysiloxane polymer (i), which are designed to interact with the Si-H groups, are preferably unsaturated groups (e.g. alkenyl terminated e.g. ethenyl terminated, propenyl terminated, allyl terminated ($\text{CH}_2=\text{CHCH}_2-$)) or terminated with acrylic or alkylacrylic such as $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}_2-$ groups. Representative, non-limiting examples of the alkenyl groups are shown by the following structures; $\text{H}_2\text{C}=\text{CH}-$, $\text{H}_2\text{C}=\text{CHCH}_2-$, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2-$, $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2-$, $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}_2-$, and $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$. Representative, non-limiting examples of alkynyl groups are shown by the following structures; $\text{HC}\equiv\text{C}-$, $\text{HC}\equiv\text{CCH}_2-$, $\text{HC}\equiv\text{CC}(\text{CH}_3)-$, $\text{HC}\equiv\text{CC}(\text{CH}_3)_2-$, $\text{HC}\equiv\text{CC}(\text{CH}_3)_2\text{CH}_2-$. Alternatively, the unsaturated organic group can be an organofunctional hydrocarbon such as an acrylate, methacrylate and the like such as alkenyl an/or alkynyl groups. Alkenyl groups are particularly preferred.

[0079] Organopolysiloxane polymer (i) is preferably a straight chain and/or branched organopolysiloxane comprising units of formula (1c)



wherein each R''' may be the same or different and is R' as hereinbefore described and a is as hereinbefore described. No R''' groups may be hydrogen groups. Preferably each R''' is the same or different and are exemplified by, but not limited to alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, undecyl, and octadecyl; cycloalkyl such as cyclohexyl; aryl such as phenyl, tolyl, xylyl, benzyl, and 2-phenylethyl; and halogenated hydrocarbon groups such as 3,3,3-trifluoropropyl, 3-chloropropyl, and dichlorophenyl.

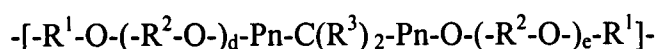
[0080] The organic oligomer (ii) as hereinbefore described may comprise any suitable organic based monomer, oligomer and/or polymer suitable as a constituent of the addition polymerisation polymer backbone. For example the organic oligomer (ii) may comprise any of organic compounds depicted as extenders and/or plasticisers above for the polycondensation polymerisation route as discussed below. In each case the oligomers used for organic oligomer (ii) comprise at least two substituent groups which

will react with the reactive group(s) of the siloxane containing material. Typically the organic oligomer (ii) comprises at least two unsaturated terminal groups, preferably alkenyl terminal groups available for interaction with e.g. Si-H groups of the siloxane containing material. Additional organic based oligomers (ii) which may be utilised include acetylene terminated oligophenylenes, vinylbenzyl terminated aromatic polysulphones oligomers. Further organic polymeric backbones suitable as oligomer (b) include aromatic polyester based monomers and aromatic polyester based monomers, both preferably comprising alkenyl terminal groups.

- 10 **[0081]** Perhaps the most preferred oligomer (ii) are polyoxyalkylene based polymers as described above with respect to the polycondensation route but in this instance the polyoxyalkylene based polymers have unsaturated (e.g. alkenyl) terminal groups instead of condensable end groups. Such polyoxyalkylene polymers again preferably comprise a linear predominantly oxyalkylene polymer comprised of recurring
- 15 oxyalkylene units, $(-C_bH_{2b}-O-)$ illustrated by the average formula $(-C_bH_{2b}-O-)_c$ wherein b and c are as hereinbefore described. The average molecular weight of each polyoxyalkylene polymer (b) may range from about 300 to about 10,000. Moreover, the oxyalkylene units are not necessarily identical throughout the polyoxyalkylene monomer, but can differ from unit to unit. A polyoxyalkylene block, for example, can
- 20 be comprised of oxyethylene units, $(-C_2H_4-O-)$; oxypropylene units $(-C_3H_6-O-)$; or oxybutylene units, $(-C_4H_8-O-)$; or mixtures thereof.

[0082] Other polyoxyalkylene monomers having unsaturated (e.g. alkenyl) terminal groups suitable for use as oligomer (b) may include for example:-

25



in which Pn, R^1 , R^2 , R^3 , d and e are as hereinbefore described.

- 30 **[0083]** Linear copolymers formed by the polymerisation of siloxane containing material in combination with oligomer (b) when oligomer (b) is a polyoxyalkylene is of a size wherein the average molecular weight of each siloxane block being is from

about 100 to about 10,000; the average molecular weight of each polyoxyalkylene block being from about 50 to about 10,000; said siloxane blocks constituting from about 20 to about 50 weight per cent of the copolymer; the polyoxyalkylene blocks constituting about 80 to about 50 weight per cent of the copolymer; and the block
5 copolymer having an average molecular weight of at least about 5,000, preferably above 15000.

[0084] The linkage between the two different copolymeric blocks resulting from the addition copolymerisation reaction in accordance with the present invention are
10 generally non-hydrolysable, comprising a divalent organic group attached to the adjacent silicon atom by a carbon to silicon bond and when (b) is a polyoxyalkylene, to the polyoxyalkylene block by an oxygen atom. Such linkages are readily apparent and determined by the reaction employed to produce the e.g. siloxane-polyoxyalkylene block copolymer. Moreover, these linear (AB)_n block copolymers
15 are also end-blocked, generally with the residual reactive groups of the reactants used to produce the linear block (AB)_n copolymers unless end-blocking compounds are introduced into the reaction mixture

[0085] Hence linear non-hydrolyzable (AB)_n block copolymers in accordance with
20 the present invention of this invention can be prepared by platinum catalyzed hydrosilation of alkenyl terminated polyethers with SiH-terminated dialkylsiloxane fluids. The resulting copolymer being a combination of polyoxyalkylene blocks linked through silicon to carbon to oxygen linkages (i.e. a propyleneoxy group) and the end-blocking groups being selected from the group consisting of allyl, propenyl
25 and/or hydrogen (dialkyl) siloxy groups (dependent on the relative amounts of the constituents which are present).

[0086] This preferred method for preparing non-hydrolyzable linear (AB)_n silicone-polyoxyalkylene block copolymers having average molecular weights ranging from at
30 least about 30,000 involves the platinum catalyzed hydrosilylation of allyl terminated polyethers with SiH-terminated dihydrocarbyl siloxane fluids. Of course it is understood that the reactants are preferably in as pure as form as possible and that the

general process requires equimolar quantities or as near to this as possible, since deviations from the 1:1 stoichiometry will not yield as high a molecular weight block copolymer as desired. However, when allyl terminated polyalkylene compounds are used an excess of said allyl compound may be desirable to allow for isomerisation of the allyl group to propenyl.

[0087] The linear siloxane-polyoxyalkylene block copolymers can have an average molecular weight of about 30,000 on up to about 250,000 or higher. The upper limit is not critical, its value merely being dependent upon the practicalities of process limitations in preparing such high molecular weight (AB)_n type polymers. The siloxane blocks of said block copolymers can constitute about 20 to about 50 weight per cent of the block copolymer, while the polyoxyalkylene blocks can constitute about 80 to about 50 weight per cent of the block copolymer. Preferably the non-hydrolyzable type (AB)_n polymers in accordance with the present invention have a number average molecular weight of at least about 30,000.

[0088] Preferably the polymer produced in accordance with the polyaddition process has an average number molecular weight (M_n) greater than 132,000 and a degree of polymerisation of greater than 1800 as determined by ASTM D5296-05 with the weight values being determined in terms of polystyrene molecular weight equivalents.

[0089] It is to be understood that while said (AB)_n block copolymers of this invention can be discrete chemical compounds they are usually mixtures of various discrete block copolymers species due at least in part to the fact that the siloxane and polyoxyalkylene reactants used to produce said (AB)_n block copolymers are themselves usually mixtures.

[0090] In carrying out the process it is generally preferred to mix all of the ingredients including the extender and/or plasticiser together at about room temperature (25°C) and allow the reaction to proceed at elevated temperatures, preferably about 60°C to about 150°C. Lower or higher temperatures up to 200°C may be employed depending on the extender and/or plasticiser being used, but there

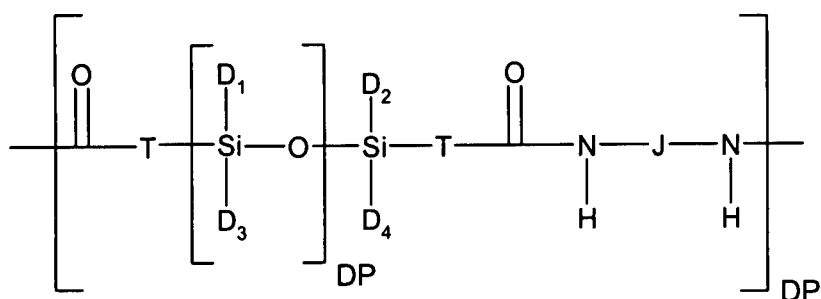
normally is no advantage. Likewise the reaction is generally conducted at atmospheric pressures, although other pressures could be used if desired. The removal or neutralization of the platinum catalyst, e.g. chloroplatinic acid is desirable and can be accomplished in any conventional manner.

5

[0091] Of course as is readily apparent to those skilled in the art the choice of the particular hydrogen terminated siloxane polymer and allyl terminated polyoxyalkylene diol reactant merely depends on the particular block copolymer desired. Moreover the final molecular weight of the block copolymer product is also
 10 a function of reaction time and temperature. Thus those skilled in the art will readily recognize that it is obvious that an extremely large number and variety of block copolymers can be predetermined and selectively prepared by routine experimentation, which permits tailoring the compositions and products made therefrom to individual specifications and needs rather than vice versa.

15

[0092] The silicone block copolymer in accordance with the present invention may alternatively having at least one repeating polyether-amide unit represented by the formula



20 wherein

T is a linear or branched C₁-C₃₀ alkylene chain;

J is a divalent organic group containing at least one polyoxyalkylene group having the formula -(C_vH_{2v}O)_x - or one polyalkylene group having the formula - (C_vH_{2v})_x - ,

25

where v is 2 to 4 inclusive, x is 1 to 700,

D¹ to D⁴ are independently a monovalent organic group;

Each DP is independently an integer having a value of 1-500;

[0093] The viscosity of the organopolysiloxanes which may be produced by the process using a catalyst according to the present invention may be in the range of
5 from 1000 to many millions mPa.s at 25°C, depending on the reaction conditions and raw materials used in the method of the invention.

[0094] The process according to the invention can be used to make a whole range of organopolysiloxane containing polymers, including liquid siloxane polymers and
10 gums of high molecular weight and viscosities of from for example from 1×10^4 to 100×10^9 mPa.s at 25°C. The molecular weight of silicone polymers is effected by the concentration of end groups, stoichiometry of the reagents. The catalyst used in the present invention has sufficient activity to enable the formation of polymers in a reasonable time at a low catalyst concentration.

15

[0095] When the addition reaction chosen is a hydrosilylation reaction, any suitable hydrosilylation catalyst may be utilised. Such hydrosilylation catalysts are illustrated by any metal-containing catalyst which facilitates the reaction of silicon-bonded hydrogen atoms of the SiH terminated organopolysiloxane with the unsaturated
20 hydrocarbon group on the polyoxyethylene. The metals are illustrated by ruthenium, rhodium, palladium, osmium, iridium, or platinum.

[0096] Hydrosilylation catalysts are illustrated by the following; chloroplatinic acid, alcohol modified chloroplatinic acids, olefin complexes of chloroplatinic acid,
25 complexes of chloroplatinic acid and divinyltetramethyldisiloxane, fine platinum particles adsorbed on carbon carriers, platinum supported on metal oxide carriers such as $\text{Pt}(\text{Al}_2\text{O}_3)$, platinum black, platinum acetylacetonate, platinum(divinyltetramethyldisiloxane), platinumous halides exemplified by PtCl_2 , PtCl_4 , $\text{Pt}(\text{CN})_2$, complexes of platinumous halides with unsaturated compounds
30 exemplified by ethylene, propylene, and organovinylsiloxanes, styrene hexamethyldiplatinum, Such noble metal catalysts are described in US Patent 3,923,705, incorporated herein by reference to show platinum catalysts. One preferred platinum

catalyst is Karstedt's catalyst, which is described in Karstedt's US Patents 3,715,334 and 3,814,730, incorporated herein by reference. Karstedt's catalyst is a platinum divinyl tetramethyl disiloxane complex typically containing one weight percent of platinum in a solvent such as toluene. Another preferred platinum catalyst is a reaction product of chloroplatinic acid and an organosilicon compound containing terminal aliphatic unsaturation. It is described in US Patent 3,419,593, incorporated herein by reference. Most preferred as the catalyst is a neutralized complex of platinum chloride and divinyl tetramethyl disiloxane, for example as described in US Patent 5,175,325.

[0097] Ruthenium catalysts such as $\text{RhCl}_3(\text{Bu}_2\text{S})_3$ and ruthenium carbonyl compounds such as ruthenium 1,1,1-trifluoroacetylacetonate, ruthenium acetylacetonate and triruthenium dodecacarbonyl or a ruthenium 1,3-ketoenolate may alternatively be used.

[0098] Other hydrosilylation catalysts suitable for use in the present invention include for example rhodium catalysts such as $[\text{Rh}(\text{O}_2\text{CCH}_3)_2]_2$, $\text{Rh}(\text{O}_2\text{CCH}_3)_3$, $\text{Rh}_2(\text{C}_8\text{H}_{15}\text{O}_2)_4$, $\text{Rh}(\text{C}_5\text{H}_7\text{O}_2)_3$, $\text{Rh}(\text{C}_5\text{H}_7\text{O}_2)(\text{CO})_2$, $\text{Rh}(\text{CO})[\text{Ph}_3\text{P}](\text{C}_5\text{H}_7\text{O}_2)$, $\text{RhX}^4_3[(\text{R}^{13})_2\text{S}]_3$, $(\text{R}^{14}_3\text{P})_2\text{Rh}(\text{CO})\text{X}^4$, $(\text{R}^{14}_3\text{P})_2\text{Rh}(\text{CO})\text{H}$, $\text{Rh}_2\text{X}^4_2\text{Y}^4_4$, $\text{H}_a\text{Rh}_b\text{olefin}_c\text{Cl}_d$, $\text{Rh}(\text{O}(\text{CO})\text{R}^{13})_{3-n}(\text{OH})_n$ where X^4 is hydrogen, chlorine, bromine or iodine, Y^4 is an alkyl group, such as methyl or ethyl, CO, C_8H_{14} or 0.5 C_8H_{12} , R^{13} is an alkyl radical, cycloalkyl radical or aryl radical and R^{14} is an alkyl radical an aryl radical or an oxygen substituted radical, a is 0 or 1, b is 1 or 2, c is a whole number from 1 to 4 inclusive and d is 2, 3 or 4, n is 0 or 1. Any suitable iridium catalysts such as $\text{Ir}(\text{OOCCH}_3)_3$, $\text{Ir}(\text{C}_5\text{H}_7\text{O}_2)_3$, $[\text{Ir}(\text{Z}^3)(\text{En})_2]_2$, or $(\text{Ir}(\text{Z}^3)(\text{Dien}))_2$, where Z^3 is chlorine, bromine, iodine, or alkoxy, En is an olefin and Dien is cyclooctadiene may also be used.

[0099] Additional components can be added to the hydrosilylation reaction which are known to enhance such reactions. These components include salts such as sodium acetate which have a buffering effect in combination with platinum catalysts.

[0100] The amount of hydrosilylation catalyst that is used is not narrowly limited as long as there is a sufficient amount to accelerate a reaction between the polyoxyethylene having an unsaturated hydrocarbon group at each molecular terminal and the SiH terminated organopolysiloxane at room temperature or at temperatures
5 above room temperature. The exact necessary amount of this catalyst will depend on the particular catalyst utilized and is not easily predictable. However, for platinum-containing catalysts the amount can be as low as one weight part of platinum for every one million weight parts of components the polyoxyethylene having an unsaturated hydrocarbon group at each molecular terminal and the SiH terminated
10 organopolysiloxane. The catalyst can be added at an amount 10 to 120 weight parts per one million parts of components the polyoxyethylene having an unsaturated organic group at each molecular terminal and the SiH terminated organopolysiloxane, but is typically added in an amount from 10 to 60 weight parts per one million parts of the polyoxyethylene having an unsaturated organic group at each molecular terminal
15 and the SiH terminated organopolysiloxane.

[0101] When the siloxane containing material is an organopolysiloxane having at least two Si-H groups, typically, the process is carried out using approximately a 1:1 molar ratio of $\equiv\text{Si-H}$ containing polysiloxane and the material containing
20 unsaturation. It is expected that useful materials may also be prepared by carrying out the process with an excess of either the $\equiv\text{Si-H}$ containing polysiloxane or the material containing unsaturation, but this would be considered a less efficient use of the materials. Typically, the material containing the unsaturation is used in slight excess to ensure all the SiH is consumed in the reaction.

[0102] A small degree of chemical reaction may occur between the OH groups in any such extender and/or plasticiser and Si-H bonds in the compounds involved in the polyaddition process used to prepare the polymer. However, because of the preferential reaction kinetics of the hydrosilylation reaction between alkenyl groups and Si-H groups
30 such interactions will kept to a minimum.

[0103] However, in the present embodiment of the invention where required an end-blocking compound may be additionally introduced into the polymerisation process to regulate the molecular weight of the polymer and/or add functionality. The same silane end-blocking compounds may be used again to introduce –OH or hydrolysable groups as end groups in polymers prepared by this polyaddition reaction pathway. In this instance the unsaturated group reacting with the end group of the polymer. However, the end-blocking compound could alternatively include Si-H groups for reaction with the polymer but this is less preferred. Any –OH or hydrolysable may be introduced in the manner. End groups which could be introduced include for example –Si(OH)₃, (R^a)Si(OH)₂, –(R^a)₂SiOH, –R^aSi(OR^b)₂, –Si(OR^b)₃, –R^a₂SiOR^b or –R^a₂ Si –R^c–SiR^d_n(OR^b)_{3-n} as discussed above.

[0104] Suitable end-blocking compounds include dialkylalkenylalkoxy silane or a dialkylalkenylsilanol. Examples of such silanes are dimethyl vinylmethoxysilane, methyl vinyl dimethoxysilane, methyl phenyl vinyl ethoxysilane and in the case where alkenyl end groups are required suitable end-blocking compounds include, for example alkenyl silazanes. Hydrolysable end blockers for the polyaddition process include, for the sake of example, alkenyltrialkoxysilanes such as vinyltrimethoxysilane and hexenyltrimethoxysilane.

CHAIN EXTENSION

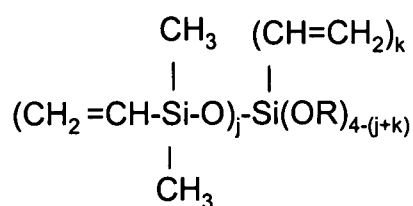
[0105] In this case rather than adding chain extender into a final pre-prepared polymer composition the extender is mixed into the polymer during a chain extension polymerisation step prior to the introduction of the other constituents of the composition. Typically the polymeric starting material is an organopolysiloxane having end groups suitable for interaction with the chosen chain extending materials. Typically the polymer end groups are either hydrolysable or suitable for addition reaction (typically hydrosilylation) and the chain extending material is chosen on the basis of having suitable reactive groups which will chain extend the polymer. Preferred chain extending materials for chain extending polymers having hydroxyl

and/or hydrolysable end groups are the monomers and/or oligomers as hereinbefore described with respect to polycondensation.

[0106] For pre-formed polymers with alkenyl or Si-H end groups suitable for addition reactions via a hydrosilylation route chain extender include for example:-

- A silane comprising two alkenyl groups, a dihydrosilane, a polydialkylsiloxane having a degree of polymerisation of from 2 to 25 and at least one Si-alkenyl bond per terminal group,
- A polydialkylsiloxane having a degree of polymerisation of from 2 to 25 and at least one Si-H bond per terminal group and wherein each alkyl group independently comprises from 1 to 6 carbon atoms;;

organosilicon compounds with the general formula



in which R is as hereinbefore described, j is 1, 2, or 3, k is 0 or 1, and $j+k$ is 2 or 3.

exemplified by compounds with the following formulas, $(\text{ViMe}_2\text{SiO})_2\text{SiVi}(\text{OMe})_1$,
 $(\text{ViMe}_2\text{SiO})_1\text{SiVi}(\text{OMe})_2$, $(\text{ViMe}_2\text{SiO})_2\text{SiVi}(\text{OEt})_1$,
 $(\text{ViMe}_2\text{SiO})_1\text{SiVi}(\text{OEt})_2$, $(\text{ViMe}_2\text{SiO})_3\text{Si}(\text{OMe})_1$,
 $(\text{ViMe}_2\text{SiO})_2\text{Si}(\text{OMe})_2$, $(\text{ViMe}_2\text{SiO})_3\text{Si}(\text{OEt})_1$ and $(\text{ViMe}_2\text{SiO})_2\text{Si}(\text{OEt})_2$

As used herein, Vi represents a vinyl group, Me represents a methyl group, and Et represents an ethyl group.

[0107] The catalyst used to catalyse the chain extension reaction is determined by the reaction to take place. When the reaction occurring is a condensation reaction any suitable condensation catalyst as hereinbefore described may be utilised. When the

reaction occurring is a hydrosilylation reaction any suitable hydrosilylation catalyst as hereinbefore described may be utilised.

5 [0108] Where required the polymer contains hydrolysable terminal groups, end-blocking agents as described above in relation to condensation may be utilised to obtain appropriate terminal groups. Where required the polymer contains addition reactable terminal groups, end-blocking agents as described above in relation to polyaddition may be utilised to obtain appropriate terminal groups.

10 [0109] The process can be carried out either batchwise or continuously on any suitable mixers. In case of a polycondensation, generated water can either be removed by chemical drying using e.g. hydrolysable silanes like methyltrimethoxysilane or by physical separation using evaporation, coalescing or centrifuging techniques.

15

[0110] Chain extension may take place at any suitable temperature and pressure for the process concerned in batch or continuous modes of operation as preferred. Hence in the case of the phosphazene catalysed methods polymerisation may occur at temperatures of between 50°C to 200°C, more preferably 80°C to 160°C.

20 Furthermore, in order to facilitate removal of the by-products formed during the condensation, for example, water, HCl or alcohol, the condensation and/or equilibration of the organosilicon compounds may be carried out at a pressure below 80 kPa. Alternative methods for the removal of condensation by-products include removal by chemical drying using e.g. hydrolysable silanes like

25 methyltrimethoxysilane (where appropriate) or by physical separation using evaporation, coalescing or centrifuging techniques.

[0111] The process can be carried out either batchwise or continuously on any suitable mixers. In case of a polycondensation, generated water can either be

30 removed by chemical drying using e.g. hydrolysable silanes like methyltrimethoxysilane or by physical separation using evaporation, coalescing or centrifuging techniques.

EXTENDER AND/OR PLASTICISER

[0112] Any suitable extender and/or plasticiser may be utilised.

5

In the case of a polycondensation polymerisation process the extender(s) and/or plasticisers do not contain any groups which may become involved in a condensation reaction with the polymer, intermediates or monomers and/or oligomers, i.e. they do not contain any OH groups or condensable groups such as alkoxy groups. Preferably
10 each extender and/or plasticiser comprises at least two unsaturated groups per molecule which will not be involved in the polymerisation process.

[0113] Preferred extenders/plasticisers for polycondensation polymerisation processes have two or more sterically unhindered unsaturated groups include organic
15 compounds such as , for example, polystyrene and/or substituted polystyrenes such as poly(α -methylstyrene), poly(vinylmethylstyrene), poly(p-trimethylsilylstyrene), polybutadiene, isoprene, linear and or branched α Ω dienes (which may be optionally substituted, examples include 1,5-hexadiene and 1,7-octadiene and poly(p-trimethylsilyl- α -methylstyrene) or organopolysiloxanes with at least two alkenyl or alkynyl groups,
20 natural oils which comprise suitable reactive groups such as linseed oil, safflower oil, tung oil, soya oil, sunflower oil, rape oil and/or castor oil. Such sterical unhindered aspect is not required where the plasticiser/extender is to be cured by a peroxide cure system.

25 **[0114]** In the case of condensation polymerisation processes, if required condensation specific catalysts are utilised to ensure no interaction with the extender/plasticiser can occur during polymerisation.

[0115] The extenders and/or plasticisers utilised in the polyaddition polymerisation in
30 accordance with this invention preferably do not contain any unsaturated groups or groups containing Si-H bonds. Preferably they comprise organic diols or organic compounds containing at least two hydrolysable groups preferably alkoxy groups.

Examples include polypropylene glycols, polyethylene glycols, poly(1,4-butanediols), organic diols such as 1,16-hexadecanediol, 1,12-dodecanediol hydroxy end-blocked siloxanes (containing no unsaturated groups) natural oils containing no unsaturation but at least two -OH groups such as castor oil.

5 Other possible extenders include saturated polyoxyalkylene based diols which preferably comprise recurring oxyalkylene units illustrated by the average formula $(-C_bH_{2b}-O-)_c$ wherein b is an integer from 2 to 4 inclusive and c is an integer of at least four. The average molecular weight of each polyoxyalkylene polymer block may range from about 300 to about 10,000. Moreover, the oxyalkylene units are not
10 necessarily identical throughout the polyoxyalkylene monomer, but can differ from unit to unit. A polyoxyalkylene block, for example, can be comprised of oxyethylene units, $(-C_2H_4-O-)$; oxypropylene units $(-C_3H_6-O-)$; or oxybutylene units, $(-C_4H_8-O-)$; or mixtures thereof. Further additional plasticiser/extenders are silanol end blocked saturated organic polymers. Mixtures of any of the above may be included.

15

[0116] A small degree of chemical reaction may occur between the OH groups in any such extender and/or plasticiser and Si-H bonds in the compounds involved in the polyaddition process used to prepare the polymer. However, because of the preferential reaction kinetics of the hydrosilylation reaction between alkenyl groups and Si-H groups
20 such interactions will kept to a minimum.

[0117] For chain extension polymerisation routes any suitable extender and/or plasticiser may be utilised dependent of the reaction scheme utilised for the chain extension mechanism. Extenders and/or plasticisers as hereinbefore described may be
25 utilised during condensation and or polyaddition chain extension processes.

[0118] Such compounds therefore effectively act as unreactive extenders and/or plasticisers during the polymerisation process as they are unable to chemically react into the polymer, intermediates or monomers/oligomers involved in the polymerisation
30 process.

[0119] The amount of extender and/or plasticiser which may be included in the composition will depend upon factors such as the purpose to which the composition is to be put, the molecular weight of the extender(s) and/or plasticiser(s) concerned etc. In general however, the higher the molecular weight of the extender(s) and/or plasticisers, the less will be tolerated in the composition but such high molecular weight extenders have the added advantage of lower volatility thus enabling the sealant composition to meet ISO 10563 requirements. Typical compositions will contain up to 70%w/w extender(s) and/or plasticisers. More suitable polymer products comprise from 5-60%w/w of linear extender(s) and/or plasticiser(s).

[0120] The polymer resulting from the polycondensation process in accordance with the invention herein is a diluted polymer comprising a siloxane based polymer having at least two unsaturated groups (preferably at least two alkenyl or alkynyl groups) per molecule and an extender and/or plasticiser comprising at least one, preferably two or more sterically unhindered unsaturated groups (unless to be cured by a peroxide based system), which is/are reactable into the cross-linked matrix formed during cure of the polymer composition into which it is introduced.

[0121] The polymer resulting from the polyaddition process in accordance with the invention herein is a diluted polymer comprising a siloxane based polymer end-blocked with at least two OH containing groups or otherwise hydrolysable groups unsaturated groups (preferably at least two OH or alkoxy groups) per molecule and an extender and/or plasticiser comprising at least one, preferably two or more sterically unhindered OH or alkoxy groups, which is/are reactable into the cross-linked matrix formed during cure of the polymer composition into which it is introduced.

[0122] The polymer resulting from the chain extension process in accordance with the invention herein is a diluted polymer comprising a siloxane based polymer having at least two reactive end groups determined by the polymerisation reaction scheme utilised and an extender and/or plasticiser comprising at least one, preferably two or more sterically unhindered groups which is/are reactable into the cross-linked matrix formed during cure of the polymer composition into which it is introduced.

[0123] As hereinbefore described the composition prepared in accordance with the present invention into which such a diluted polymer is introduced contains the said diluted polymer, filler and a suitable cure system to form a curable composition.

5

[0124] Any suitable filler or combination of fillers may be utilised. The compositions may contain one or more finely divided, reinforcing fillers (e) such as high surface area fumed and precipitated silicas and to a degree calcium carbonate or additional non-reinforcing fillers such as crushed quartz, diatomaceous earths, barium sulphate, iron oxide, titanium dioxide and carbon black, talc, wollastonite. Other fillers which might be used alone or in addition to the above include aluminite, calcium sulphate (anhydrite), gypsum, calcium sulphate, magnesium carbonate, clays such as kaolin, aluminium trihydroxide, magnesium hydroxide (brucite), graphite, copper carbonate, e.g. malachite, nickel carbonate, e.g. zarachite, barium carbonate, e.g. witherite and/or strontium carbonate e.g. strontianite

15

[0125] 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; $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$; grossular; and $\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{12}$. Aluminosilicates comprise ground silicate minerals, such as but not limited to, sillimanite; Al_2SiO_5 ; mullite; $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$; kyanite; and Al_2SiO_5 . The ring silicates group comprises silicate minerals, such as but not limited to, cordierite and $\text{Al}_3(\text{Mg,Fe})_2[\text{Si}_4\text{AlO}_{18}]$. The chain silicates group comprises ground silicate minerals, such as but not limited to, wollastonite and $\text{Ca}[\text{SiO}_3]$.

25

[0126] The sheet silicates group comprises silicate minerals, such as but not limited to, mica; $\text{K}_2\text{Al}_4[\text{Si}_6\text{Al}_2\text{O}_{20}](\text{OH})_4$; pyrophyllite; $\text{Al}_4[\text{Si}_8\text{O}_{20}](\text{OH})_4$; talc; $\text{Mg}_6[\text{Si}_8\text{O}_{20}](\text{OH})_4$; serpentine for example, asbestos; Kaolinite; $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$; and vermiculite.

30

[0127] In addition, a surface treatment of the filler(s) may be performed, for example with a fatty 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 sealant components. The surface treatment of the fillers makes the ground silicate minerals easily wetted by the silicone polymer. These surface modified fillers do not clump, and can be homogeneously incorporated into the silicone polymer. This results in improved room temperature mechanical properties of the uncured compositions. Furthermore, the surface treated fillers give a lower conductivity than untreated or raw material.

[0128] The proportion of such fillers when employed will depend on the properties desired in the elastomer-forming composition and the cured elastomer. Usually the filler content of the composition will reside within the range from about 5 to about 500 parts by weight per 100 parts by weight of the polymer excluding the extender portion.

[0129] The curing package utilised is determined by the reactive groups contained in the polymers produced in step one described above.

[0130] Polymers produced by both polycondensation and polyaddition reaction pathways either route discussed may be cured using organic peroxides such as dialkyl peroxides, diphenyl peroxides, benzoyl peroxide, 1,4-dichlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, di-*t*-butyl peroxide, dicumyl peroxide, tertiary butyl-perbenzoate, monochlorobenzoyl peroxide, ditertiary-butyl peroxide, 2,5-bis-(tertiarybutyl-peroxy)-2,5-dimethylhexane, tertiary-butyl-trimethyl peroxide, tertiary-butyl-tertiary-butyl-tertiary-triphenyl peroxide, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, and *t*-butyl perbenzoate. The most suitable peroxide based curing agents are benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, di-*t*-butyl peroxide, and dicumyl peroxide. Such organic peroxides are used at up to 10 parts per 100 parts of the combination of polymer, filler and optional additives. Preferably between 0.2 and 2 parts of peroxide are used.

[0131] The present compositions containing polymers having two more unsaturated groups can also be cured and/or cross-linked by a hydrosilylation reaction catalyst in combination with an organohydrogensiloxane as the curing agent. In the case of hydrosilylation cure systems substantially all the polymer must, comprise a majority of polymer molecules which contain at least two unsaturated groups suitable for cross-linking with the organohydrogensiloxane. The unsaturated groups are typically alkenyl groups, most preferably vinyl groups.

[0132] It will be appreciated that extenders and/or plasticisers containing at least one and preferably two or more unsaturated groups per molecule which merely functioned as a substantially unreactive diluent in the condensation polymerisation process as hereinbefore described in the cure process is chemically bound into the cross-linked matrix therefore preventing substantial weight loss. Indeed in the case where the extender and/or plasticiser comprises 2 unsaturated groups it functions as a chain extender in the cure process in accordance with the present invention.

[0133] To effect curing of the present composition, the organohydrogensiloxane cross-linker must contain more than two silicon bonded hydrogen atoms per molecule. The organohydrogensiloxane can contain, for example, from about 4-20 silicon atoms per molecule, and but could have a viscosity of up to about 10 Pa.s at 25°C. The silicon-bonded organic groups present in the organohydrogensiloxane can include substituted and unsubstituted alkyl groups of 1-4 carbon atoms that are otherwise free of ethylenic or acetylenic unsaturation. The organohydrogensiloxane which functions as a cross-linker contains an average of at least two silicon-bonded hydrogen atoms per molecule, and no more than one silicon-bonded hydrogen atom per silicon atom, the remaining valences of the silicon atoms being satisfied by divalent oxygen atoms or by monovalent hydrocarbon radicals comprising one to seven carbon atoms. The monovalent hydrocarbon radicals can be, for examples, alkyls such as methyl, ethyl, propyl, tertiary butyl, and hexyl; cycloalkyls such as cyclohexyl; and aryls such as phenyl and tolyl. Such materials are well known in the art. The molecular structure of the organohydrogensiloxane may be linear, linear

including branching, cyclic, or network-form or mixture thereof. There are no particular restrictions on the molecular weight of the organohydrogensiloxane, however it is preferable that the viscosity at 25°C be 3 to 10,000 mPa.s. Furthermore, the amount of cross-linker that is added to the composition is an amount such that the ratio of the number of moles of hydrogen atoms bonded to silicon atoms to the number of moles of alkenyl groups in the polymer and extender/plasticiser is in the range of 0.5:1 to 20:1, and preferably in the range of 1:1 to 5:1. If this molar ratio is less than 0.5, curing of the present composition becomes insufficient, while if this molar ratio exceeds 20 hydrogen gas is evolved so that foaming occurs.

[0134] Preferably any hydrosilylation catalyst as hereinbefore described may be utilised, although platinum based catalysts are preferred.

[0135] In this case curing such compositions the hydrosilylation catalyst may be added to the present composition in an amount equivalent to as little as 0.001 part by weight of elemental platinum group metal, per one million parts (ppm) of the composition. Preferably, the concentration of the hydrosilylation catalyst in the composition is that capable of providing the equivalent of at least 1 part per million of elemental platinum group metal. A catalyst concentration providing the equivalent of about 3-50 parts per million of elemental platinum group metal is generally the amount preferred.

[0136] Optionally when the cure catalyst is a hydrosilylation catalyst particularly a platinum based catalyst a suitable hydrosilylation catalyst inhibitor may be required.

Any suitable platinum group type inhibitor may be used. One useful type of platinum catalyst inhibitor is described in U.S. Pat. No. 3,445,420, which is hereby incorporated by reference to show certain acetylenic inhibitors and their use. A preferred class of acetylenic inhibitors are the acetylenic alcohols, especially 2-methyl-3-butyn-2-ol and/or 1-ethynyl-2-cyclohexanol which suppress the activity of a platinum-based catalyst at 25°C. A second type of platinum catalyst inhibitor is described in U.S. Pat. No. 3,989,667, which is hereby incorporated by reference to show certain olefinic siloxanes, their preparation and their use as platinum catalyst

inhibitors. A third type of platinum catalyst inhibitor includes polymethylvinylcyclsiloxanes having three to six methylvinylsiloxane units per molecule.

5 [0137] In the case where the polymer and extender/plasticiser both comprise OH groups or other hydrolysable groups (and the latter at least contains no unsaturated groups) then the cure package is a suitable condensation cure package comprising a cross-linker and appropriate condensation catalyst.

10 [0138] Any suitable cross-linker for condensation (i.e. moisture) cure may be used. The cross-linker used in the moisture curable composition as hereinbefore described is preferably a silane compound containing hydrolysable groups. These include one or more silanes or siloxanes which contain silicon bonded hydrolysable groups such as acyloxy groups (for example, acetoxy, octanoyloxy, and benzyloxy groups);
15 ketoximino groups (for example dimethyl ketoximo, and isobutylketoximino); alkoxy groups (for example methoxy, ethoxy, and propoxy) and alkenyloxy groups (for example isopropenyloxy and 1-ethyl-2-methylvinylloxy).

[0139] In the case of siloxane based cross-linkers the molecular structure can be
20 straight chained, branched, or cyclic.

[0140] The moisture cure cross-linker may have two but preferably has three or four silicon-bonded condensable (preferably hydrolysable) groups per molecule. When the cross-linker is a silane and when the silane has three silicon-bonded hydrolysable
25 groups per molecule, the fourth group is suitably a non-hydrolysable silicon-bonded organic group. These silicon-bonded organic groups are suitably hydrocarbyl groups which are optionally substituted by halogen such as fluorine and chlorine. Examples of such fourth groups include alkyl groups (for example methyl, ethyl, propyl, and butyl); cycloalkyl groups (for example cyclopentyl and cyclohexyl); alkenyl groups
30 (for example vinyl and allyl); aryl groups (for example phenyl, and tolyl); aralkyl groups (for example 2-phenylethyl) and groups obtained by replacing all or part of the

hydrogen in the preceding organic groups with halogen. Preferably however, the fourth silicon-bonded organic groups is methyl.

[0141] Silanes and siloxanes which can be used as cross-linkers include
5 alkyltrialkoxysilanes such as methyltrimethoxysilane (MTM) and
methyltriethoxysilane, alkenyltrialkoxysilanes such as vinyltrimethoxysilane and
vinyltriethoxysilane, isobutyltrimethoxysilane (iBTM). Other suitable silanes include
ethyltrimethoxysilane, vinyltriethoxysilane, phenyltrimethoxysilane,
alkoxytrioximosilane, alkenyltrioximosilane, , 3,3,3-trifluoropropyltrimethoxysilane,
10 methyltriacetoxysilane, vinyltriacetoxysilane, ethyl triacetoxysilane, di-butoxy
diacetoxysilane, phenyl-tripropionoxysilane, methyltris(methylethylketoximo)silane,
vinyl-tris-methylethylketoximo)silane, methyltris(methylethylketoximino)silane,
methyltris(isopropenoxy)silane, vinyltris(isopropenoxy)silane, ethylpolysilicate, n-
propylorthosilicate, ethylorthosilicate, dimethyltetraacetoxysiloxane. The
15 cross-linker used may also comprise any combination of two or more of the above.

[0142] The amount of cross-linker present in the composition will depend upon the
particular nature of the cross-linker and in particular, the molecular weight of the
molecule selected. The compositions suitably contain cross-linker in at least a
20 stoichiometric amount as compared to the polymeric material described above.
Compositions may contain, for example, from 2-30% w/w of cross-linker, but
generally from 2 to 10% w/w. Acetoxy cross-linkers may typically be present in
amounts of from 3 to 8 %w/w preferably 4 to 6 %w/w whilst oximino cross-linkers,
which have generally higher molecular weights will typically comprise from 3-8%
25 w/w.

[0143] The composition further comprises a condensation catalyst. This increases
the speed at which the composition cures. The catalyst chosen for inclusion in a
particular silicone sealant composition depends upon the speed of cure required. Any
30 suitable condensation catalyst may be utilised to cure the composition. Particularly
preferred catalysts for curing the moisture curable composition are the tin, lead,
antimony, iron, cadmium, barium, manganese, zinc, chromium, cobalt, nickel,

titanium, aluminium, gallium or germanium and zirconium based catalysts such as organic tin metal catalysts and 2-ethylhexoates of iron, cobalt, manganese, lead and zinc may alternatively be used. Organotin, titanate and/or zirconate based catalysts as hereinbefore described.

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[0144] Other ingredients which may be included in the compositions include but are not restricted to co-catalysts for accelerating the cure of the composition such as metal salts of carboxylic acids and amines; rheological modifiers; Adhesion promoters, pigments, Heat stabilizers, Flame retardants, UV stabilizers, cure
10 modifiers, electrically and/or heat conductive fillers, Fungicides and/or biocides and the like (which may suitably be present in an amount of from 0 to 0.3% by weight), water scavengers, (typically the same compounds as those used as cross-linkers or silazanes). It will be appreciated that some of the additives are included in more than one list of additives. Such additives would then have the ability to function in all the
15 different ways referred to.

[0145] The rheological additives include silicone organic co-polymers such as those described in EP 0802233 based on polyols of polyethers or polyesters; non-ionic surfactants selected from the group consisting of polyethylene glycol, polypropylene
20 glycol, ethoxylated castor oil, oleic acid ethoxylate, alkylphenol ethoxylates, copolymers or ethylene oxide (EO) and propylene oxide (PO), and silicone polyether copolymers; as well as silicone glycols. For some systems rheological additives, particularly copolymers of ethylene oxide (EO) and propylene oxide (PO), and silicone polyether copolymers may enhance the adhesion of the sealant to substrates,
25 particularly plastic substrates.

[0146] Any suitable adhesion promoter(s) may be incorporated in a sealant composition in accordance with the present invention. These may include for example alkoxy silanes such as aminoalkylalkoxy silanes, epoxyalkylalkoxy silanes,
30 for example, 3-glycidoxypropyltrimethoxysilane and, mercapto-alkylalkoxy silanes and γ -aminopropyl triethoxysilane, reaction products of ethylenediamine with silylacrylates. Isocyanurates containing silicon groups such as 1,3,5-

tris(trialkoxysilylalkyl) isocyanurates may additionally be used. Further suitable adhesion promoters are reaction products of epoxyalkylalkoxy silanes such as 3-glycidoxypyrroltrimethoxysilane with amino-substituted alkoxysilanes such as 3-aminopropyltrimethoxysilane and optionally alkylalkoxy silanes such as methyl-
5 trimethoxysilane. epoxyalkylalkoxy silane, mercaptoalkylalkoxy silane, and derivatives thereof.

[0147] Heat stabilizers may include Iron oxides and carbon blacks, Iron carboxylate salts, cerium hydrate, barium zirconate, cerium and zirconium octoates, and
10 porphyrins.

[0148] Flame retardants may include for example, carbon black, hydrated aluminium hydroxide, and silicates such as wollastonite, platinum and platinum compounds.
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[0149] Electrically conductive fillers may include carbon black, metal particles such as silver particles any suitable, electrically conductive metal oxide fillers such as titanium oxide powder whose surface has been treated with tin and/or antimony, potassium titanate powder whose surface has been treated with tin and/or antimony,
20 tin oxide whose surface has been treated with antimony, and zinc oxide whose surface has been treated with aluminium.

[0150] Thermally conductive fillers may include metal particles such as powders, flakes and colloidal silver, copper, nickel, platinum, gold aluminium and titanium, metal oxides, particularly aluminium oxide (Al_2O_3) and beryllium oxide (BeO);magnesium oxide, zinc oxide, zirconium oxide; Ceramic fillers such as tungsten monocarbide, silicon carbide and aluminium nitride, boron nitride and diamond.
25

[0151] Any suitable Fungicides and biocides may be utilised, these include N-substituted benzimidazole carbamate, benzimidazolylcarbamate such as methyl 2-benzimidazolylcarbamate, ethyl 2-benzimidazolylcarbamate, isopropyl 2-
30

benzimidazolylcarbamate, methyl N-{2-[1-(N,N-dimethylcarbamoyl)benzimidazolyl]} carbamate, methyl N-{2-[1-(N,N-dimethylcarbamoyl)-6-methylbenzimidazolyl]} carbamate, methyl N-{2-[1-(N,N-dimethylcarbamoyl)-5-methylbenzimidazolyl]} carbamate, methyl N-{2-[1-(N-methylcarbamoyl)benzimidazolyl]} carbamate, methyl N-{2-[1-(N-methylcarbamoyl)-6-methylbenzimidazolyl]} carbamate, methyl N-{2-[1-(N-methylcarbamoyl)-5-methylbenzimidazolyl]} carbamate, ethyl N-{2-[1-(N,N-dimethylcarbamoyl)benzimidazolyl]} carbamate, ethyl N-{2-[2-(N-methylcarbamoyl)benzimidazolyl]} carbamate, ethyl N-{2-[1-(N,N-dimethylcarbamoyl)-6-methylbenzimidazolyl]} carbamate, ethyl N-{2-[1-(N-methylcarbamoyl)-6-methylbenzimidazolyl]} carbamate, isopropyl N-{2-[1-(N,N-dimethylcarbamoyl)benzimidazolyl]} carbamate, isopropyl N-{2-[1-(N-methylcarbamoyl)benzimidazolyl]} carbamate, methyl N-{2-[1-(N-propylcarbamoyl)benzimidazolyl]} carbamate, methyl N-{2-[1-(N-butylcarbamoyl)benzimidazolyl]} carbamate, methoxyethyl N-{2-[1-(N-propylcarbamoyl)benzimidazolyl]} carbamate, methoxyethyl N-{2-[1-(N-butylcarbamoyl)benzimidazolyl]} carbamate, ethoxyethyl N-{2-[1-(N-propylcarbamoyl)benzimidazolyl]} carbamate, ethoxyethyl N-{2-[1-(N-butylcarbamoyl)benzimidazolyl]} carbamate, methyl N-{1-(N,N-dimethylcarbamoyloxy)benzimidazolyl]} carbamate, methyl N-{2-[N-methylcarbamoyloxy)benzimidazolyl]} carbamate, methyl N-{2-[1-(N-butylcarbamoyloxy)benzimidazolyl]} carbamate, ethoxyethyl N-{2-[1-(N-propylcarbamoyl)benzimidazolyl]} carbamate, ethoxyethyl N-{2-[1-(N-butylcarbamoyloxy)benzimidazolyl]} carbamate, methyl N-{2-[1-(N,N-dimethylcarbamoyl)-6-chlorobenzimidazolyl]} carbamate, and methyl N-{2-[1-(N,N-dimethylcarbamoyl)-6-nitrobenzimidazolyl]} carbamate. 10, 10'-oxybisphenoxarsine (trade name: Vinyzene, OBPA), di-iodomethyl-para-tolylsulfone, benzothiophene-2-cyclohexylcarboxamide-S,S-dioxide, N-(fluordichloridemethylthio)phthalimide (trade names: Fluor-Folper, Preventol A3). Methyl-benzimideazol-2-ylcarbamate (trade names: Carbendazim, Preventol BCM), Zinc-bis(2-pyridylthio-1-oxide) (zinc pyrithion) 2-(4-thiazolyl)-benzimidazol, N-phenyl-iodpropargylcarbamate, N-octyl-4-isothiazolin-3-on, 4,5-dichloride-2-n-octyl-4-isothiazolin-3-on, N-butyl-1,2-

benzisothiazolin-3-on and/or Triazolyl-compounds, such as tebuconazol in combination with zeolites containing silver.

5 [0152] Other optional ingredients which may be incorporated in the composition of a high consistency silicone rubber include handling agents, peroxide cure co-agents, acid acceptors, and UV stabilisers.

10 [0153] Handling agents are used to modify the uncured properties of the silicone rubber such as green strength or processability sold under a variety of trade names such as SILASTIC® HA-1, HA-2 and HA-3 sold by Dow Corning corporation)

15 [0154] Peroxide cure co-agents are used to modify the properties, such as tensile strength, elongation, hardness, compression set, rebound, adhesion and dynamic flex, of the cured rubber. These may include di- or tri-functional acrylates such as Trimethylolpropane Triacrylate and Ethylene Glycol Dimethacrylate; Triallyl Isocyanurate, Triallyl Cyanurate, Polybutadiene oligomers and the like. Silyl-hydride functional siloxanes may also be used as co-agents to modify the peroxide catalysed cure of siloxane rubbers.

20 [0155] The acid acceptors may include Magnesium oxide, calcium carbonate, Zinc oxide and the like.

25 [0156] The ceramifying agents can also be called ash stabilisers and include silicates such as wollastonite.

30 [0157] The silicone rubber composition in accordance with this embodiment may be made by any suitable route, for example one preferred route is to first make a silicone rubber base by heating a mixture of fumed silica, a treating agent for the silica, and the diluted organopolysiloxane containing polymer of the present invention. The silicone rubber base is removed from the first mixer and transferred to a second mixer where generally about 150 parts by weight of a non-reinforcing or extending filler such as ground quartz is added per 100 parts by weight of the silicone rubber base.

Other additives are typically fed to the second mixer such as curing agents, pigments and colouring agents, heat stabilizers, anti-adhesive agents, plasticizers, and adhesion promoters. In a second preferred route the diluted organopolysiloxane containing polymer of the present invention and any desired filler plus any desired treating agent
5 are fed into a reactor and mixed, further additives as described above including cure agents are then fed into the same reactor and further mixed.

[0158] Hence in a further embodiment of the present invention there is provided an extended and/or plasticised organopolysiloxane composition capable of cure to an
10 elastomeric body, the composition comprising

A polysiloxane containing polymer

Filler and

a suitable first cure system adapted to cure the polymer and optionally
15 at least one extender and/or plasticiser reactable with the cure system so as to participate in the formation of an elastomeric cross-linked matrix with the polymer upon curing.

[0159] In a still further embodiment of the present invention there is provided an
20 extended and/or plasticised organopolysiloxane composition capable of cure to an elastomeric body obtainable in accordance with the following steps:-

(i) Preparing an extended and/or plasticised polysiloxane containing polymer by intermixing the polymer and/or precursors thereof with an extender and/or
25 plasticiser and optionally filler during or subsequent to polymerisation of the polysiloxane containing polymer

(ii) Mixing the resulting polysiloxane containing polymer product with:
Any remaining filler and
30 a suitable first cure system to form a curable composition;
characterised in that the extender and/or plasticiser is chemically functionalised so as to substantially not participate in any chemical reaction(s) with the polymer and/or its

precursors during step (i) or step (ii) but is chemically attached to the cross-linked matrix of the resulting cured elastomer during curing.

5 [0160] The compositions provided in accordance with the present invention are made in accordance with any method as hereinbefore described and may comprise any combination of components hereinbefore described as well as any additive or combination of additives as hereinbefore described.

10 [0161] Elastomers prepared from silicone rubber compositions in accordance with the present invention may be used in a wide variety of applications including in the manufacture of for example:- automotive, aviation and aerospace products, baby care products such as teats for bottles, insulators for power and utilities applications, extruded profiles, gaskets and seals for e.g. air water, fuel and oil applications e.g. hoses, keypads, in medical and office equipment such as protective equipment and
15 masks, rollers for e.g. photocopiers, sponges, and wire and cable coating applications.

[0162] The invention will now be described by way of Example.

EXAMPLES

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[0163] In the following examples all viscosity measurements relating to organopolysiloxane polymers were taken at 25°C.

COMPARATIVE EXAMPLE 1

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[0164] A Winkworth Z-blade mixer was loaded with 1200g of a 70 durometer polydimethylsiloxane elastomer composition, comprising

- 35 parts by weight dimethylvinyl siloxy terminated dimethyl siloxane gum, having a plasticity of from 55 to 65 mils
- 30 • 27 parts by weight dimethylvinyl siloxy terminated dimethyl methylvinyl siloxane gum, having a plasticity of from 55 to 65 mils

- 1 parts by weight of hydroxy-terminated dimethyl methylvinyl siloxane having a viscosity of 20 mPa.s at 25°C.
- 5 parts by weight of hydroxy-terminated dimethyl siloxane having a viscosity of about 21 mPa.s at 25°C
- 5 • 34 parts by weight of fumed silica

[0165] This was allowed to mix on its own for several minutes at ambient temperature. A total of 300g of an unreactive hydrocarbon extender (Hydrotreated Middle Distillates (Petroleum - Pilot 900, Petrochem Carless)) was then added over
10 the course of several hours (~6hrs). This gave a master batch (MB1) consisting of 80% by weight of the elastomer composition and 20% by weight of extender.

[0166] Samples were then prepared, on a two roll mill, at different concentrations of extender by introducing varying amounts of the 70 durometer polydimethylsiloxane
15 composition described above (extender free) into MB1. A hydrosilylation curing system was added in the amounts indicated in Table 1 below. Each resulting sample was cured for 10 minutes at 130 °C to give a test sheet which was tested as indicated in Table 1 below

TABLE 1:

Run	1	2	3	4
MB1 parts	100	50	25	0
70 duro elastomer parts	0	50	75	100
Platinum Vinyl siloxane complex masterbatch in siloxane (~0.1% w/w Pt) parts	0.9	0.9	0.9	0.9
Poly-dimethyl-methylhydrogen-siloxane copolymer master batch in siloxane (~0.16% w/w SiH as H) parts	5	5	5	5
1-Ethynyl-1-cyclohexanol master batch in siloxane (10% w/w) parts	2.2	2.2	2.2	2.2
Tensile Strength (ISO 37: 1994 Type 2) (MPa)	7.7	8.8	9.3	9.7
Elongation at Break (ISO 34: 1994 Type 2) (%)	858	765	747	711
Hardness (BS ISO EN 868:2003) (Durometer Shore A)	38.3	52.1	57.8	65.5
Tear Strength (ASTM 624 -98, Die B) (kNm ⁻¹)	55.8	53.9	52.0	50.8
Density (kg/m ³)	1.104	1.147	1.170	1.197
Mass loss on heating 24h @ 200 °C (%)	22.3	12.4	7.5	2.0
Mass loss on Toluene extraction (%)	21.2	15.2	8.6	4.5

- 5 **[0167]** The test used to measure Mass Loss on Heating was as follows:-

A 6mm x 26mm disk was cut from the test sheet and weighed; it was then suspended in a circulating oven at 200°C for 24 hours, allowed to cool and reweighed. Mass loss is quoted as a percent of the original mass.

- 10 **[0168]** The test used to measure Mass Loss on Toluene Extraction was as follows:-

A 2mm x 26mm disk was cut from the test sheet and weighed; it was then placed in 5ml of toluene at room temperature and left shaking for 8 hours then left standing overnight. The disk was dried in air at ambient temperatures for 24 hours then an oven at 100°C for 24 hours, allowed to cool and reweighed. Mass loss is quoted as a percent of the original mass.

[0169] The results for Mass Loss on Heating and Mass Loss on Toluene extraction clearly show that the hydrocarbon extender does not react with the silicone during cure and is readily removed from the cured product.

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COMPARATIVE EXAMPLE 2

[0170] The same method as for Comparative Experiment 1 was used except that a trimethylsilyl end-blocked polydimethylsiloxane, (Viscosity ~ 100,000mPa.s at 25°C) was used as a plasticiser to prepare the masterbatch (MB2). Mixing was more rapid than in comparative example 1 (~2hrs). Samples were prepared as shown in Table 2. Samples were cured for 10 minutes at 130 °C to give a test sheet which was tested according to the procedures shown in TABLE 2

15

TABLE 2:

Run	1	2	3	4
MB2	100	50	25	0
70 duro elastomer parts	0	50	75	100
Platinum Vinyl siloxane complex masterbatch in siloxane (~0.1% w/w Pt) parts	0.9	0.9	0.9	0.9
Poly-dimethyl-methylhydrogen-siloxane copolymer master batch in siloxane (~0.16% w/w SiH as H) parts	5	5	5	5
1-Ethynyl-1-cyclohexanol master batch in siloxane (10% w/w) parts	2.2	2.2	2.2	2.2
Tensile Strength (ISO 37: 1994 Type 2) (MPa)	9.9	9.8	10.0	9.7
Elongation at Break (ISO 34: 1994 Type 2) (%)	783	696	680	711
Hardness (BS ISO EN 868:2003) (Durometer Shore A)	40.4	53.0	58.9	65.5
Tear Strength (ASTM 624 -98, Die B) (kNm ⁻¹)	51.3	50.0	48.8	50.8
Density (kg/m ³)	1.144	1.167	1.180	1.197
Mass loss on heating 24h @ 200 °C (%)	2.0	1.9	1.9	2.0

Mass loss on Toluene extraction (%)	10.7	5.9	4.3	4.5
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[0171] Whilst the trimethylsilyl end-blocked polydimethylsiloxane is of sufficiently high molecular weight to be physically trapped within the cured elastomeric matrix and is not lost upon post cure heating, it is clear that substantially none of the extender chemically react into the cured elastomeric matrix and therefore such extenders may be extracted by solvent extraction as shown in Table 2 above.

COMPARATIVE EXAMPLE 3

[0172] The same method as described in Comparative Experiment 1 was used except that a vinyltrimethylsilyl end-blocked polydimethylsiloxane ($M_p = 101000$, $M_n = 57100$, Degree of polymerisation (DP) of about 770) was used as extender to prepare a masterbatch (MB3). Mixing was more rapid than in Comparative Example 1 (~2hrs). Samples were prepared as shown in TABLE 3. Samples were cured for 10 minutes at 130 °C to give a test sheet which was tested according to the procedures shown in TABLE 3.

TABLE 3:

Run	1	2	3	4
MB3	100	50	25	0
70 duro elastomer parts	0	50	75	100
Platinum Vinyl siloxane complex masterbatch in siloxane (~0.1% w/w Pt) parts	0.9	0.9	0.9	0.9
Poly-dimethyl-methylhydrogen-siloxane copolymer master batch in siloxane (~0.16% w/w SiH as H) parts	5	5	5	5
1-Ethynyl-1-cyclohexanol master batch in siloxane (10% w/w) parts	2.2	2.2	2.2	2.2
Tensile Strength (ISO 37: 1994 Type 2) (MPa)	9.9	9.2	9.6	9.7

Elongation at Break (ISO 34: 1994 Type 2) (%)	630	625	669	711
Hardness (BS ISO EN 868:2003) (Durometer Shore A)	50.3	57.6	61.5	65.5
Tear Strength (ASTM 624 -98, Die B) (kNm ⁻¹)	38.8	48.5	52.5	50.8
Density (kg/m ³)	1.1418	1.1675	1.1796	1.1970
Mass loss on heating 24h @ 200 °C (%)	1.9	1.9	1.9	2.0
Mass loss on Toluene extraction (%)	3.2	3.2	3.0	4.5

[0173] Whilst the vinyl dimethylsilyl end-blocked polydimethylsiloxane is of sufficiently high molecular weight that it cannot be removed by heating it is clear that a large portion of the extender does now react into the cured elastomeric matrix and cannot be removed by solvent extraction. However it is to be appreciated that it required a period of 6 hours mixing in order for the extender to be fully blended into the pre-prepared gum. Therefore whilst the blending of a reactive extender offers benefits in that reduction in durometer with extender loading is less than in the cases where the extender is non reactive (Comparative Example 1 and 2), the time required for mixing the extender into the gum is unacceptable.

EXAMPLE 4

[0174] A mixture of a silanol end-blocked polydimethylsiloxane, (Siloxane A, Mp = 4500, Mn = 2400, DP ~ 30, Viscosity ~ 70 mPa.s at 25°C) 50 parts with a vinyl end-blocked polydimethylsiloxane diluent, (Siloxane B, Mp = 24100, Mn = 12200, DP ~ 160, Viscosity ~ 450 mPa.s at 25°C) 50 parts was prepared. Dodecylbenzene sulphonic Acid, 1 part by weight vs. total siloxane content was then added and thoroughly mixed into the mixture to catalyse the condensation polymerisation of Siloxane A. After 24hr at room temperature the extended polymer product was neutralised with Calcium Carbonate and analysed by Gel Permeation Chromatography. The results in Table 4 show that Siloxane A has reacted to give a high molecular weight product (Mp 94600) whilst Siloxane B has remained substantially unchanged throughout the reaction as desired for use as extender.

TABLE 4:

Material	Mp	Mn	Mw	Polydispersity
Siloxane A	4500	2400	4900	2.02
Siloxane B (Extender)	24100	12200	22100	1.80
Reaction Product	94600, 26300 (Two peaks)	11500 (Average for both peaks)	60100 (Average for both peaks)	5.23 (Average for both peaks)

EXAMPLE 5

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EXAMPLE 5.1

[0175] A mixture of 79.5 parts by weight of Siloxane A, (as described above) was mixed with 0.5 parts by weight of a second silanol end-blocked poly-dimethyl-methylvinylsiloxane copolymer (Siloxane D, ~4 DP, 11% Vi by weight) and 20 parts by weight of a vinyl end-blocked polydimethylsiloxane diluent, (Siloxane C, Mn = 57100, DP ~ 770, Viscosity ~ 55000 mPa.s at 25°C) was prepared and charged to a Brabender plasticorder mixer. Dodecylbenzene sulphonic Acid, 5 parts by weight vs. total siloxane, was then added and well mixed, after 45 minutes at room temperature, the reaction was neutralised with Magnesium Oxide and analysed by Gel Permeation Chromatography. The product was found to have Mn = 133000, Mw = 392000.

EXAMPLE 5.2

[0176] To the product from Example 5.1 was added 40 parts pyrogenic silica (Cab-O-Sil® MS-75D, Surface Area 255 m²/g), 10 parts of a silanol end-blocked polydimethylsiloxane ~10 DP and 1 part of a silanol end-blocked poly-dimethyl-methylvinylsiloxane copolymer (~4 DP, 11% Vi by weight). The mixture was heated

to 130 °C with constant mixing at 20 rpm and held for 1 hour. The product was cooled.

Example 5.2a: Part of the cooled product was mixed with 2phr of a paste of
5 Dichlorobenzoyl peroxide (50 parts in silicone oil) on a two roll mill and cured 5 minutes at 116 °C under 2MPa pressure in a suitable mould to give a test sheet.

Example 5.2b Part of the cooled product was mixed with 0.9 parts of a Vinyl
siloxane – Platinum complex (0.12% Pt by weight); 1 part of a
10 Dimethylmethylhydrogen siloxane copolymer (15 cSt, 0.85% SiH as H) and 0.22 parts of 1-Ethynyl-1-Cyclohexanol on a two roll mill and cured 10 minutes at 150 °C under 2MPa pressure in a suitable mould to give a test sheet.

The physical properties of the rubbers produced are provided in Table 5 below:-

TABLE 5

Example	5.2a	5.2b
Cure System	Peroxide	Pt
Tensile Strength (ISO 37: 1994 Type 2)	9.1 MPa	9.4 MPa
Elongation at Break (ISO 34: 1994 Type 2)	646%	800%
Durometer Shore A (BS ISO EN 868:2003)	36	37
Tear (ASTM 624 -98, Die B)	46 kN/m	34 kN/m

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EXAMPLE 6

[0177] A mixture of Siloxane A, 80 parts with a vinyl end-blocked polydimethylsiloxane diluent, (Siloxane C, $M_p = 101000$, $M_n = 57100$, $DP \sim 770$, Viscosity ~ 55000 mPa.s at) 20 parts was prepared and charged to a Brabender plasticorder mixer. Dodecylbenzene sulphonic Acid (Bio-Soft 101), 5 part by weight vs. total siloxane, was then added and well mixed, after 120 minutes at room temperature, the reaction was neutralised with Magnesium Oxide and analysed by Gel Permeation Chromatography. The product was found to have $M_n = 115000$, $M_w = 300000$.

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[0178] Example 6.2 - Preparation of a Treated Kaolin Filled Silicone Rubber

To the product of Example 6.1 was added 100 parts of a methyltrimethoxysilane treated calcined Kaolin prepared according to methods described in WO 2005/054352. The mix was mixed in a Brabender plasticorder mixer at 20 rpm for 90 minutes. The product was cooled and mixed with 2phr of a paste of Dichlorobenzoyl peroxide 50 parts in silicone oil on a two roll mill and cured 5 minutes at 116 °C to give a test sheet which was tested according to the following procedures.

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TABLE 6

Tensile Strength (ISO 37: 1994 Type 2) (MPa)	4.7
Elongation at Break (ISO 34: 1994 Type 2) (%)	285
Hardness (BS ISO EN 868:2003) (Durometer Shore A)	48
Tear Strength (ASTM 624 -98, Die B) (kNm⁻¹)	17.9

- 5 **[0179]** Comparison of these properties with those of a typical silicone rubber (Kirk-Othmer Encyclopaedia of Chemical Technology, John Wiley & Sons, Inc) shows that the above example provides a useful silicone rubber composition without the issues normally associated with the production and handling of a high molecular weight siloxane gum. It is also worth noting that addition of a silanol end-blocked poly-
- 10 dimethyl-methylvinylsiloxane copolymer during preparation of the polymer, Example 5.2 results in a material with enhanced tear properties.

EXAMPLE 7**EXAMPLE 7.1 COMPARATIVE**

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- [0180]** A mixture of 79.5 parts by weight of Siloxane A, (as described above) was mixed with 0.5. parts of a second silanol end-blocked poly-dimethyl-methylvinylsiloxane copolymer (Siloxane D, ~4 DP, 11% Vi by weight) and 20 parts by weight of a trimethylsiloxy end-blocked polydimethylsiloxane diluent, (Siloxane
- 20 E, Viscosity 10,000 cS at 25 °C) was prepared and charged to a Brabender plasticorder mixer. Dodecylbenzene sulphonic Acid, 5 parts by weight vs. total siloxane, was then added and well mixed, after 90 minutes at room temperature, the reaction was neutralised with Magnesium Oxide.

- 25 **[0181]** To this product was added 100 parts of a methyltrimethoxysilane treated calcined Kaolin prepared according to methods described in WO 2005/054352. The mix was mixed in a Brabender plasticorder mixer at 20 rpm for 90 minutes. The

cooled product was mixed with 0.9 parts of a Vinyl siloxane – Platinum complex (0.12% Pt by weight); 1 part of a Dimethylmethylhydrogen siloxane copolymer (15 cSt, 0.85% SiH as H) and 0.22 parts of 1-Ethynyl-1-Cyclohexanol on a two roll mill and cured 10 minutes at 150 °C under 2MPa pressure in a suitable mould to give a test sheet.

[0182] Polymer A contains pendant vinyl groups and in this example the extender contains no groups which react with the monomers/oligomers or resulting polymer as the polymer is produced via a condensation polymerisation route. However, in this comparative example the extender is also not involved in the cure process as it contains no groups which will take part in a hydrosilylation cure process.

EXAMPLE 7.2

[0183] A mixture of 79.5 parts by weight of Siloxane A, (as described above) was mixed with 0.5 parts of a second silanol end-blocked poly-dimethyl-methylvinylsiloxane copolymer (Siloxane D, ~4 DP, 11% Vi by weight) and 20 parts by weight of a vinyl end-blocked polydimethylsiloxane extender, (Siloxane F, Viscosity 9,500 cS at 25 °C) was prepared and charged to a Brabender plasticorder mixer. Dodecylbenzene sulphonic Acid, 5 parts by weight vs. total siloxane, was then added and well mixed, after 90 minutes at room temperature, the reaction was neutralised with Magnesium Oxide.

[0184] To this product was added 100 parts of a methyltrimethoxysilane treated calcined Kaolin prepared according to methods described in WO 2005/054352. The mix was mixed in a Brabender plasticorder mixer at 20 rpm for 90 minutes. The cooled product was mixed with 0.9 parts of a Vinyl siloxane – Platinum complex (0.12% Pt by weight); 1 part of a Dimethylmethylhydrogen siloxane copolymer (15 cSt, 0.85% SiH as H) and 0.22 parts of 1-Ethynyl-1-Cyclohexanol on a two roll mill and cured 10 minutes at 150 °C under 2MPa pressure in a suitable mould to give a test sheet.

[0185] In this case whilst Polymer A contains pendant vinyl groups and in this example the extender contains vinyl groups which will not react with the monomers/oligomers or resulting polymer as the polymer is produced via a condensation polymerisation route. However, in this example the extender
5 participates in the cure process as it contains vinyl groups which will take part in a hydrosilylation cure process.

[0186] The physical properties of the resulting products are depicted in Table 7

Example	7.1 Comparative	7.2
Tensile Strength (ISO 37: 1994 Type 2)	1.6 MPa	3.3 MPa
Elongation at Break (ISO 34: 1994 Type 2)	222 %	265 %
Durometer Shore A (BS ISO EN 868:2003)	14	32
Tear (ASTM 624 -98, Die B)	6.9 kN/m	8.9 kN/m
Toluene Extractables (48h RT)	16.8%	5.9%

This example again shows that having vinyl functionality on both the polymer and diluent (Example 7.2) gives both superior properties and lower extractables.

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TYPICAL PROPERTIES OF SILICONE RUBBERS

Hardness, durometer	25-80
Tensile strength, MPa	4.1-11.0
Elongation %	100-700

CLAIMS

1. A method for the production of an extended and/or plasticised organopolysiloxane composition comprising the steps:-

Mixing a polysiloxane containing polymer and/or precursors thereof With:-

an extender and/or plasticiser prior to and/or during polymerisation of the polysiloxane containing polymer and/or

Filler during or subsequent to polymerisation of the polysiloxane containing polymer and

and optionally introducing residual extender and/or plasticiser and/or filler together with a first cure package for curing the polymer subsequent to polymerisation characterised in that the extender and/or plasticiser is chemically functionalised so as to substantially not participate in any chemical reaction(s) with the polymer and/or its precursors, prior to cure, but is chemically attached to the cross-linked matrix of the resulting cured elastomer during curing.

2. A method for the production of a cured organopolysiloxane based elastomer comprising the steps of
 - (i) Preparing an extended and/or plasticised polysiloxane containing polymer by intermixing the polymer and/or precursors thereof with an extender and/or plasticiser and optionally filler, prior to and/or during polymerisation of the polysiloxane containing polymer
 - (ii) Mixing the resulting extended and/or plasticised polysiloxane containing polymer product with:
a suitable cure system to form a curable composition; and optionally filler;
and
 - (iii) curing the resulting polymer composition to form a cured elastomer having a cross-linked matrix;

characterised in that the extender and/or plasticiser is chemically functionalised so as to substantially not participate in any chemical reaction(s) with the polymer and/or its precursors during steps (i) or (ii) but is chemically attached to the cross-linked matrix of the resulting cured elastomer during curing

3. A method for the production of an extended and/or plasticised organopolysiloxane composition comprising the steps:-
 - (i) Preparing an extended and/or plasticised polysiloxane containing polymer by intermixing the polymer and/or precursors thereof with an extender and/or plasticiser and optionally filler, prior to and/or during polymerisation of the polysiloxane containing polymer
 - (ii) Mixing the resulting polysiloxane containing polymer product with:
a suitable first cure system and optionally filler to form a curable composition;
characterised in that the extender and/or plasticiser is chemically functionalised so as to substantially not participate in any chemical reaction(s) with the polymer and/or its precursors during step (i) or step (ii) but is chemically attached to the cross-linked matrix of the resulting cured elastomer during curing.
4. A method in accordance with any one of claims 1 to 3 characterised in that the extended and/or plasticised polysiloxane containing polymer comprises hydrolysable end groups and pendant unsaturated groups.
5. A method in accordance with any one of claims 1, 2 or 3 characterised in that extended and/or plasticised polysiloxane containing polymer is prepared by means of a polymerisation process wherein siloxane containing monomers and/or oligomers are polymerised in the presence of
the extender and/or plasticiser,

a suitable catalyst and
optionally an end-blocking agent; and

Where required quenching the polymerisation process.

6. A method in accordance with claim 4 or 5 characterised in that the polymerisation process is a polycondensation process and the catalyst is a condensation catalyst.
7. A method in accordance with claim 4, 5 or 6 characterised in that each siloxane containing monomer and/or oligomer comprises at least two condensable groups selected from –OH groups and alkoxy groups having from 1 to 10 carbon atoms.
8. A method in accordance with claim 4, 5, 6 or 7 characterised in that the extended and/or plasticised polysiloxane containing polymer produced contains at least two unsaturated organic groups having from 2 to 10 carbon atoms per molecule.
9. A method in accordance with claim 8 characterised in that the unsaturated groups are introduced into the extended and/or plasticised polysiloxane containing polymer by the inclusion of an end-blocking agent into the reaction mixture during polymerisation.
10. A method in accordance with any one of claims 5 to 9 characterised in that the extender and/or plasticiser contains at least two organic unsaturated groups having from 2 to 10 carbon atoms and no condensable groups.
11. A method in accordance with claims 8 or 10 characterised in that the unsaturated groups are alkenyl groups or alkynyl groups.
12. A method in accordance with any one of claims 6 to 11 characterised in that the cure system comprises a hydrosilylation cure package comprising a organohydrogensiloxane and a hydrosilylation catalyst.

13. A method in accordance with claim 5 characterised in that the polymerisation process is a polyaddition process.
14. A method in accordance with claim 13 in that the polyaddition process is a hydrosilylation polymerisation process.
15. A method in accordance with claim 14 characterised in that at least 50% of the siloxane containing monomers and/or oligomers comprise at least two unsaturated organic groups having from 2 to 10 carbon atoms per molecule and the remaining siloxane containing monomers and/or oligomers comprise at least two Si-H bonds per molecule.
16. A method in accordance with claim 14 or 15 characterised in that the extended and/or plasticised polysiloxane containing polymer produced contains at least two hydroxy groups or condensable groups having from 1 to 10 carbon atoms per molecule.
17. A method in accordance with claim 16 characterised in that the condensable groups are introduced into the extended and/or plasticised polysiloxane containing polymer by the inclusion of an end-blocking agent into the reaction mixture during polymerisation.
18. A method in accordance with any one of claims 13 to 17 characterised in that the extender and/or plasticiser contains at least two groups selected from hydroxyl groups and/or alkoxy groups having from 1 to 10 carbon atoms and no unsaturated groups or groups comprising Si-H bonds.
19. A method in accordance with claim 15 characterised in that the unsaturated groups are alkenyl groups or alkynyl groups.
20. A method in accordance with any one of claims 13 to 19 characterised in that the cure system comprises a condensation cure package.

21. A method in accordance with any preceding claim characterised in that the composition additionally comprises one or more additives selected from rheological modifiers; adhesion promoters, pigments, Heat stabilizers, Flame retardants, UV stabilizers, Chain extenders, electrically and/or heat conductive fillers, Fungicides and/or biocides
22. An extended and/or plasticised organopolysiloxane composition capable of cure to an elastomeric body, the composition comprising
- A polysiloxane containing polymer prepared in accordance with any one of claims 1, 2 or 3;
- Filler and
- a suitable first cure system adapted to cure the polymer and optionally at least one extender and/or plasticiser reactable with the cure system so as to participate in the formation of an elastomeric cross-linked matrix with the polymer upon curing.
23. An extended and/or plasticised organopolysiloxane composition capable of cure to an elastomeric body obtainable in accordance with the following steps:-
- (i) Preparing an extended and/or plasticised polysiloxane containing polymer by intermixing the polymer and/or precursors thereof with an extender and/or plasticiser and optionally filler prior to and/or during polymerisation of the polysiloxane containing polymer
- (ii) Mixing the resulting polysiloxane containing polymer product with:
- Any remaining filler and any residual extender
- a suitable first cure system to form a curable composition;
- characterised in that the extender and/or plasticiser is chemically functionalised so as to substantially not participate in any chemical reaction(s) with the polymer and/or its precursors during step (i) or step (ii)

but is chemically attached to the cross-linked matrix of the resulting cured elastomer during curing.

24. Use of a silicone rubber composition prepared in accordance with any one of claims 1 to 20 in the preparation of automotive, aviation and aerospace products, baby care products such as teats for bottles, insulators for power and utilities applications, extruded profiles, gaskets and seals for e.g. air water, fuel and oil applications e.g. hoses, keypads, in medical and office equipment such as protective equipment and masks, rollers for e.g. photocopiers, sponges, and wire and cable coating applications.
25. A method in accordance with any one of claims 1 to 5 characterised in that the cure system comprises an organoperoxide catalyst.