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(54) **Title:** SILICONE FOAM CONTROL AGENT

(57) **Abstract:** A method of making silicone-based foam control agents comprising: i) preparing a polysiloxane containing polymer by the polymerisation of siloxane containing monomers and/or oligomers in the presence of an inert organopolysiloxane and/or an organic fluid, a suitable catalyst and optionally an end-blocking agent; ii) where required quenching the polymerisation process; wherein the inert organopolysiloxane and/or organic fluid is substantially retained within the resulting diluted polysiloxane containing polymer; iii) introducing from 0.1 to 10 % by weight of a suitable filler prior to during or subsequent to step (i); iv) optionally introducing up to 5% by weight of a suitable silicone resin during or subsequent to step (i) and v) where required, adapting the foam control agent produced in steps (i) to (iv) into a suitable form of delivery therefor.

SILICONE FOAM CONTROL AGENT

[0001] This invention is concerned with silicone-based foam control agents, particularly for use in aqueous compositions, preferably detergent compositions.

[0002] In many aqueous systems which are used e.g. in food processes, textile dying, paper production, sewage treatment and cleaning applications, surface active agents are present either as an unwanted ingredient or as deliberately introduced materials to achieve a certain function. Due to the presence of these surface active agents foam is often generated. In certain applications, such as in dish washing by hand, this is a welcome effect but in other applications foam generation can lead to unsatisfactory results. This is for example the case in the dyeing of textiles or in the manufacture of paper. In other applications, for example the use of detergent compositions for domestic laundering, the production of foam needs to be controlled rather than avoided. It is important to keep the foam formation to an acceptable level when laundering is performed in automatic washing machines, especially front loading machines. Excessive foam would cause overflow of the washing liquor onto the floor as well as reduction in the efficiency of the laundering operation itself.

[0003] Silicone-based foam control agents are known and have been incorporated into, for example, heavy duty detergent powders and liquids for use in automatic washing machines. Silicone foam control agents are regarded as very effective in this application as they can be added in very small quantities and are not affected by e.g. the hardness of water, while traditional foam control compositions, such as soaps, require a certain water hardness for their effectiveness. However, they are usually not cheap, and there is a need to find ways to cheapen such formulations without compromising the cost-efficiency of the foam control agents.

[0004] In addition, the detergent industry is constantly going through an evolution where, due to environmental concerns, energy conservation efforts, machine design changes, water conservation and changing laundering habits there is a move towards the use of detergent compositions which will perform to a higher efficiency than hitherto. There is a need to control foam from e.g. increased surfactant levels in the detergent compositions, use of surfactants which have a higher foam profile than traditional surfactants and changing laundering conditions. Since silicone foam control agents do not directly contribute to the cleaning power of a detergent composition it is desirable to keep the addition level of such foam control agents to a minimum. There has therefore arisen a need to develop improved foam control agents for incorporation into detergent compositions.

[0005] Silicone foam control agents are mostly based on organopolysiloxane materials, which may be linear or branched, and which may contain a variety of silicon-bonded substituents. As the market for these products has developed the antifoams available have become increasingly complex and difficult and expensive to produce. The polymers used can be extremely expensive to produce because of the complex side chain technology required. EP 217501 describes a foam control agent wherein a liquid siloxane component is obtained by blending two pre-prepared polymers,:-
100 parts by weight of a polydiorganosiloxane having triorganosiloxane end-groups and a viscosity of from 3×10^{-4} m^2/s to 6×10^{-2} m^2/s at 25°C, and
10 to 125 parts of a polydiorganosiloxane having at least one terminal silanol group and at least 40 silicon atoms; with
0.5 to 10 parts of an organopolysiloxane resin comprising monofunctional and tetrafunctional siloxane units in a ratio of from 0.5:1 to 1.2:1 and having at least one silanol group per molecule and heating the resultant mixture, optionally in the presence of a suitable condensation or equilibration reaction type catalyst . The post heated mixture has a viscosity in the range of 1×10^{-2} m^2/s to 3×10^{-2} m^2/s at 25°C. The specification describes the need to control the amount of resin used in order to retain a liquid polymer, avoiding a gel structure. This indicates that some branching occurs in the siloxane component of the foam control agent.

[0006] US3,691,091 discloses a silicone emulsion for defoaming aqueous liquids, in which the silicone consists essentially of a polydimethylsiloxane fluid, silica, and an organosilicon compound or oligomer containing alkoxy and/or silanol groups.

[0007] EP0163541 describes a method for the preparation of a silicone defoamer by reacting a mixture of components including a pre-prepared polyorganosiloxane polymer bearing one or more hydroxyl and/or hydrocarbonoxy groups, a silicone resin, a filler, a catalyst to promote reaction. Optionally the composition can contain an organopolysiloxane free of reactive groups.

[0008] EP 0273448 describes a process for preparing a foam suppressant composition by reacting an organopolysiloxane together with amorphous silica and a free radical initiator catalyst and optionally a vinyl monomer and/or a vinyl modified polyorganosiloxane under conditions and for a time sufficient such that free radical polymerisation occurs and a polymerisation product forms. In this invention it is essential that the resulting product is diluted with sufficient quantities of a polydiorganosiloxane having a viscosity of 10 to 300 cSt such that the final composition has a viscosity of 100 to 10,000 cSt.

[0009] GB 2257709 describes a foam control agent which is particularly useful when incorporated in detergent compositions where a high level of high foaming surfactants is present, and comprises a branched polydiorganosiloxane which is prepared through hydrosilylation of a vinyl end-blocked polydiorganosiloxane having a viscosity of from 200 to 100 000 mPa.s at 25°C, a volatile low viscosity organohydrogensiloxane having at least 3 Si-H groups and a solvent in the presence of a noble metal catalyst. The solvent used was preferably a polydiorganosiloxane and was mainly present to solubilise the branched polydiorganosiloxane product.

[0010] GB 1224026 describes an antifoaming agent which is composed of 10 parts by weight of certain water-insoluble organic liquids and from 0.1 to 5.0 parts by weight of an organopolysiloxane which is compatible in the organic liquid and consists essentially of monovalent and tetravalent siloxane units. US3666681 describes an antifoaming agent for aqueous systems consisting essentially of a mixture of 100 parts by weight of certain water-insoluble organic liquids, from 0.5 to 10.0 parts by weight of an organopolysiloxane, which may be a fluid or a resinous compound, and from 0.5 to 10.0 parts by weight of a filler which is selected from finely divided silica and methylsilsesquioxane gel, and from 0.002 to 5.0 parts by weight of a compound which is selected from ammonia, a disilazane and an alkali or alkaline earth metal hydroxide.

[0011] EP1075863 describes a foam control agent according to the invention comprises (A) a pre-prepared organopolysiloxane polymeric material having at least one silicon-bonded substituent of the formula X-Ph, wherein X denotes a divalent aliphatic hydrocarbon group and Ph denotes an aromatic group, (B) a water-insoluble organic fluid, (C) an organosilicon resin and (D) a hydrophobic filler.

[0012] US4690713 describes an antifoam composition comprising (a) either a hydrocarbon oil or a pre-prepared polydimethylsiloxane polymer, (b) an organosilane, (c) silica filler, and (d) a suitable catalyst.

[0013] US5777059 describes a silicone composition by reacting (i) a polyisobutylene compound, (ii) a pre-prepared polyorganosiloxane polymer, (iii) an organosilane or silicone resin, (iv) a suitable catalyst and optionally a silica filler. The mixture is blended and then reacted at room temperature or with heat.

[0014] WO2005/058454 and WO2005/058455 describe foam control compositions comprising a liquid polymer of an unsaturated hydrocarbon, a branched silicone resin and a particulate filler which is insoluble in the liquid hydrocarbon polymer. WO2005/058455 further comprises a non polar organic material having a melting point of 35 to 100°C which is miscible with the organic liquid.

[0015] The high cost of producing antifoam materials can now be avoided by way of their preparation using the following process which produces satisfactory antifoam materials at a fraction of the cost of many manufacturing processes currently used.

[0016] The invention is directed to a method of making silicone-based foam control agents comprising

i) Preparing a polysiloxane containing polymer by the polymerisation of siloxane containing monomers and/or oligomers in the presence of an inert organopolysiloxane and/or an organic fluid, a suitable catalyst and optionally an end-blocking agent;
ii) Where required quenching the polymerisation process; wherein the inert organopolysiloxane and/or organic fluid,is substantially retained within the resulting diluted polysiloxane containing polymer

iii) introducing from 0.1 to 10 % by weight of a suitable filler prior to during or subsequent to step (i);
iv) optionally introducing up to 5% by weight of a suitable organosilicon resin and
v) where required, adapting the foam control agent produced in steps (i) to (iv) into a suitable form of delivery therefor.

[0017] It is to be understood that steps (iii) and (iv) may take place in any order and may, but need not, be both undertaken at the same stage in the process. Most preferably step (iv) is undertaken after step (ii) where required.

[0018] 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.

[0019] For the sake of this application an inert fluid (e.g. the inert organopolysiloxane and/or organic fluid) is intended to be unreactive towards any other constituent of step (i), (ii) and (iii) above. i.e. it does not chemically participate in the polymerisation reaction of step (i) and does not chemically interact with the additives introduced in steps (ii) and (iii). Indeed it is possible that the filler and resin of steps (ii) and (iii) respectively, may be introduced into the mixture in the form of a concentrate comprising the filler and/or resin in the inert fluid, especially if this aids processing.

[0020] A polysiloxane containing polymer is intended to mean a polymer comprising multiple organosiloxane or polyorganosiloxane groups per molecule and is intended to include a polymer substantially containing only organosiloxane or polyorganosiloxane groups in the polymer chain and polymers where the backbone contains both organosiloxane and/or polyorganosiloxane groups and e.g. organic polymeric groups in the polymeric chain. Such polymers can be homopolymers or co-polymers, including, but not limited to, block co-polymers and random co-polymers.

[0021] In accordance with the present invention a polysiloxane containing polymer which has been prepared in the presence of an inert fluid in accordance with the present invention preferably has the general formula:

$$R_{(3-a)}R^1_aSiO[(R_2SiO)_b(RR^1SiO)_c]SiR_{(3-a)}R^1_a \qquad (1)$$

wherein each R is the same or different and is an alkyl group preferably containing 1-8 carbon atoms, a substituted alkyl group preferably containing 1 to 6 carbon atoms an optionally substituted phenyl group or an optionally substituted alkylphenyl group; each R^1 is hydrogen, a hydroxy group, a hydrolysable group or an unsaturated organic group; a is zero or 1, b is an integer and c is zero or an integer and the sum of b + c is equal to a value of at least 200 preferably at least 500, more preferably at least 1500. Such a polymer may comprise a degree of branching.

[0022] For the purpose of this application "Substituted" , when used in relation to hydrocarbon groups, means one or more hydrogen atoms in the hydrocarbon group has been replaced with another substituent. Examples of such substituents include, but are not 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.

[0023] The polymeric chain may comprise blocks made from chains of units depicted in Formula (1) above where the two R groups or R and R^1 groups are

both alkyl groups (preferably both methyl or ethyl), or
alkyl and phenyl groups, or
alkyl and fluoropropyl, or
alkyl and alkenyl or
alkyl and alkylphenyl; or
alkyl and hydrogen groups.

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

[0024] Whilst preferably the polysiloxane containing polymer has a substantially organopolysiloxane molecular chain, the polysiloxane containing polymer may alternatively contain a block copolymeric backbone comprising at least one block of siloxane groups and an organic component comprising any suitable organic based polymer backbone for example the organic polymer backbone may comprise, for example, polystyrene and/or substituted polystyrenes such as poly(α-methylstyrene), poly(vinylmethylstyrene), dienes, poly(p-trimethylsilylstyrene) and poly(p-trimethylsilyl-α-methylstyrene). Other organic components which may be incorporated in the polymeric backbone may include acetylene terminated oligophenylenes, vinylbenzyl terminated aromatic polysulphones oligomers, aromatic polyesters, aromatic polyester based monomers, polyalkylenes, polyurethanes, aliphatic polyesters, aliphatic polyamides and aromatic polyamides and the like.

[0025] However perhaps the most preferred organic based polymeric blocks in polysiloxane containing polymer are polyoxyalkylene based blocks. 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. Preferably the polyoxyalkylene polymeric backbone consists essentially of oxyethylene units and/or oxypropylene units.

[0026] Other polyoxyalkylene blocks in the polysiloxane containing polymer may include for example units of the structure-

$$-[-R^2-O-(-R^3-O-)_d-Pn-C(R^4)_2-Pn-O-(-R^3-O-)_e-R^2]-$$

in which Pn is a 1,4-phenylene group, each R^2 is the same or different and is a divalent hydrocarbon group having 2 to 8 carbon atoms, each R^3 is the same or different and, is, an ethylene group propylene group or isopropylene group, each R^4 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.

[0027] In accordance with the present invention it is to be understood that the polysiloxane containing polymer is polymerised in an inert fluid. It is to be understood that the term “inert fluid” is intended to mean a substantially non-volatile fluid which is neither involved in the polymerisation process nor is removed prior to emulsification. Hence the inert fluid is substantially present in the emulsion.

[0028] Preferably the inert fluid is selected from an organopolysiloxane extender and/or plasticiser and/or an organic extender or plasticiser or a cyclic siloxane comprising between 3 and 20 silicon atoms. Preferably the inert fluid has a viscosity of from 0.65 mPa.s at 25°C - 10000 mPa.s at 25°C.

[0029] Preferably each extender and or plasticiser is miscible or at least substantially miscible with the monomeric starting materials with which they are initially mixed, and more particularly miscible 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 solids which become miscible liquids in a reaction mixture during the polymerisation process.

[0030] For the sake of this application an extender (sometimes also referred to as a process aid or secondary plasticiser) is a compound typically used to dilute silicone based compositions to make them more economically competitive without substantially negatively affecting the properties of the formulation.

[0031] Suitable inert liquids include trialkylsilyl terminated polydialkylsiloxanes and derivatives thereof which may comprise a degree of substitution, with the provision that any substituted groups in the inert fluid do not participate in the polymerisation reaction. The substituted groups on the inert fluid are preferably the same as those identified in the previous definition of substituted groups with respect to hydrocarbon groups. Preferably each alkyl group may be the same or different and comprises from 1 to 8 carbon atoms but is preferably a methyl or ethyl group, preferably with a viscosity of from 0.65 to 100 000 mPa.s at 25°C and most preferably from 10 to 1000 mPa.s at 25°C.

[0032] The inert fluid may comprise any suitable organic extender/organic plasticiser. Mineral oil extenders and plasticisers are however particularly preferred. Examples include linear or branched mono unsaturated hydrocarbons such as linear or branched alkenes or mixtures thereof containing at least 12, e.g. from 12 to 25 carbon atoms; and/or mineral oil fractions comprising linear (e.g. n-paraffinic) mineral oils, branched (iso-paraffinic) mineral oils, cyclic (referred in some prior art as naphthenic) mineral oils and mixtures thereof. Preferably the hydrocarbons utilised comprise at least 10, preferably at least 12 and most preferably greater than 20 carbon atoms per molecule.

[0033] Other preferred mineral oil extenders include alkylcycloaliphatic compounds, low molecular weight polyisobutylenes, Phosphate esters, alkybenzenes including polyalkylbenzenes which are unreactive with the polymer.

[0034] Any suitable mixture of mineral oil fractions may be utilised as the extender in the present invention but high molecular weight extenders (e.g. >220) are particularly preferred. Examples include:-

alkylcyclohexanes (molecular weight > 220); paraffinic hydrocarbons and mixtures thereof containing from 1 to 99%, preferably from 15 to 80% n-paraffinic and/or isoparaffinic hydrocarbons (linear branched paraffinic) and 1 to 99%, preferably 85 to 20% cyclic hydrocarbons (naphthenic) and a maximum of 3%, preferably a maximum of 1% aromatic carbon atoms. The cyclic paraffinic hydrocarbons (naphthenics) may contain cyclic and/or polycyclic hydrocarbons. Any suitable mixture of mineral oil fractions may be used, e.g. mixtures containing

(i) 60 to 80% paraffinic and 20 to 40% naphthenic and a maximum of 1% aromatic carbon atoms;
(ii) 30-50 %, preferably 35 to 45% naphthenic and 70 to 50% paraffinic and or isoparaffinic oils;
(iii) hydrocarbon fluids containing more than 60 wt.% naphthenics, at least 20 wt.% polycyclic naphthenics and an ASTM D-86 boiling point of greater than 235°C;
(iv) hydrocarbon fluid having greater than 40 parts by weight naphthenic hydrocarbons and less than 60 parts by weight paraffinic and/or isoparaffinic hydrocarbons based on 100 parts by weight of hydrocarbons.

[0035] Preferably the mineral oil based extender or mixture thereof comprises at least one of the following parameters:-

(i) a molecular weight of greater than 150, most preferably greater than 200;
(ii) an initial boiling point equal to or greater than 230°C (according to ASTM D 86).
(iii) a viscosity density constant value of less than or equal to 0.9; (according to ASTM 2501)
(iv) an average of at least 12 carbon atoms per molecule, most preferably 12 to 30 carbon atoms per molecule;
(v) an aniline point equal to or greater than 70°C, most preferably the aniline point is from 80 to 110°C (according to ASTM D 611);
(vi) a naphthenic content of from 20 to 70% by weight of the extender and a mineral oil based extender has a paraffinic content of from 30 to 80% by weight of the extender according to ASTM D 3238);
(vii) a pour point of from -50 to 60°C (according to ASTM D 97);
(viii) a kinematic viscosity of from 1 to 20 cSt at 40°C (according to ASTM D 445)
(ix) a specific gravity of from 0.7 to 1.1 (according to ASTM D1298) ;

(x) a refractive index of from 1.1 to 1.8.at 20°C (according to ASTM D 1218)

(xi) a density at 15°C of greater than 700kg/m^3 (according to ASTM D4052) and/or

(xii) a flash point of greater than 100°C, more preferably greater than 110°C (according to ASTM D 93)

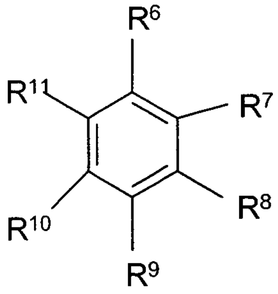
(xiii) a saybolt colour of at least +30 (according to ASTM D 156)

(xiv) a water content of less than or equal to 250ppm

(xv) a Sulphur content of less than 2.5ppm (according to ASTM D 4927)

[0036] Other organic extenders may include for the sake of example, fatty acids and fatty acid esters, alkylbenzene compounds suitable for use include heavy alkylate alkylbenzene or an alkylcycloaliphatic compound. Examples of alkyl substituted aryl compounds useful as extenders and/or plasticisers are compounds which have aryl groups, especially benzene substituted by alkyl and possibly other substituents, and a molecular weight of at least 200.

[0037] The alkylbenzene compounds suitable for use include heavy alkylate alkylbenzene or an alkylcycloaliphatic compound. Examples of alkyl substituted aryl compounds useful as extenders and/or plasticisers are compounds which have aryl groups, especially benzene substituted by alkyl and possibly other substituents, and a molecular weight of at least 200. Examples of such extenders are described in US Patent No. 4,312,801, the content of which is incorporated herein by reference. These compounds can be represented by general formula (2), (3), (4) and (5)



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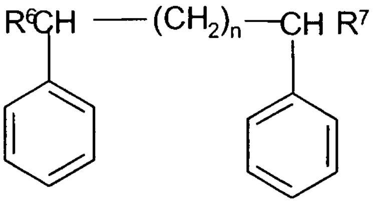

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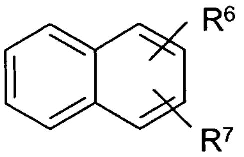

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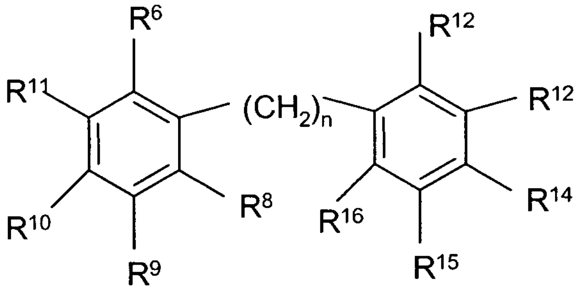
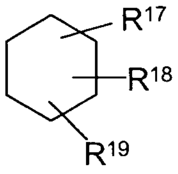


(5)

where R^6 is an alkyl chain of from 1 to 30 carbon atoms, each of R^7 through to R^{16} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, halogen, haloalkyl, nitrile, amine, amide, an ether such as an alkyl ether or an ester such as an alkyl ester group, and n is an integer of from 1 to 25. Of these compounds of formula (2) where each of R^7, R^8, R^9, R^{10} and R^{11} is hydrogen and R^6 is a C_{10}-C_{13} alkyl group are preferred. A particularly useful source of such compounds are the so-called “heavy alkylates”, which are recoverable from oil refineries after oil distillation. Generally distillation takes place at temperatures in the range of from 230 to 330°C, and the heavy alkylates are present in the fraction remaining after the lighter fractions have been distilled off.

[0038] Examples of alkylcycloaliphatic compounds are substituted cyclohexanes with a molecular weight in excess of 220. Examples of such compounds are described in EP

0842974, the content of which is incorporated herein by reference. Such compounds may be represented by general formula (6).



(6)

where R^{17} is a straight or branched alkyl group of from 1 to 25 carbon atoms, and R^{18} and R^{19} are independently selected from hydrogen or a C_{1-25} straight or branched chain alkyl group.

[0039] Alternatively the inert fluid may comprise may comprise a suitable non-mineral based (i.e. not from petroleum or petroleum based oils) natural oil or a mixture thereof, i.e. those derived from animals, seeds and nuts such as for example almond oil, avocado oil, beef tallow, borrage oil, butterfat, canola oil, cardanol, cashew nut oil, cashew nutshell liquid, castor oil, citrus seed oil, cocoa butter, coconut oil, cod liver oil, corn oil, cottonseed oil, cuphea oil, evening primrose oil, hemp oil, jojoba oil, lard, linseed oil, macadamia oil, menhaden oil, oat oil, olive oil , palm kernel oil, palm oil peanut oil, poppy seed oil, rapeseed oil, rice bran oil, safflower oil, safflower oil (high oleic), sesame oil, soybean oil, sunflower oil, sunflower oil (high oleic), tall oil, tea tree oil, turkey red oil, walnut oil perilla oil, dehydrated castor oils, apricot oil, pine nut oil, kukui nut oil, amazon nut oil almond oil, babasu oil, argan oil, black cumin oil, bearberry oil, calophyllum oil, camelina oil, carrot oil, carthamus oil, cucurbita oil, daisy oil, grape seed oil, foraha oil, jojoba oil, queensland oil, onoethera oil, ricinus oil, tamanu oil, tucuma oil, fish oils such as pilchard, sardine and herring oils. The extender may alternatively comprise mixtures of the above and/or derivatives of one or more of the above.

[0040] A wide variety of natural oil derivates are available. These include transesterified natural vegetable oils, boiled natural oils such as boiled linseed oil, blown natural oils and stand natural oils. An example of a suitable transesterified natural vegetable oil is known as biodiesel oil, the transesterification product produced by reacting mechanically extracted natural vegetable oils from seeds, such as rape, with methanol in the presence of a sodium hydroxide or potassium hydroxide catalyst to produce a range of esters dependent on the feed utilised. Examples might include for example methyloleate ($CH_3(CH_2)_7CH=CH(CH_2)_7CO_2CH_3$).

[0041] Stand natural oils which are also known as thermally polymerised or heat polymerised oils and are produced at elevated temperatures in the absence of air. The oil polymerises by cross-linking across the double bonds which are naturally present in the oil. The bonds are of the carbon-carbon type. Stand natural oils are pale coloured and low in acidity. They can be produced with a wider range of viscosities than blown oils and are more stable in viscosity. In general, stand natural oils are produced from linseed oil and soya bean oil but can also be manufactured based on other oils. Stand natural oils are widely used in the surface coatings industry.

[0042] Blown oils which are also known as oxidised, thickened and oxidatively polymerised oils and are produced at elevated temperatures by blowing air through the oil. Again the oil polymerises by cross-linking across the double bonds but in this case there are oxygen molecules incorporated into the cross-linking bond. Peroxide, hydroperoxide and hydroxyl groups are also present. Blown oils may be produced from a wider range of oils than stand natural oils. In general, blown oils are darker in colour and have a higher acidity when compared to stand natural oils. Because of the wide range of raw materials used, blown oils find uses in many diverse industries, for example blown linseed oils are used in the surface coatings industry and blown rapeseed oils are often used in lubricants.

[0043] The amount of inert fluid 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 inert fluid(s) concerned etc. Typical compositions may contain up to at least 70%w/w or even 90% w/w inert fluids(s). Preferably suitable polymer products comprise from 5 to 80%w/w of inert fluid(s).

[0044] Such polysiloxane containing polymers as prepared in step (i) of the process in accordance with the present invention may be made by a variety of routes with the polymers produced being end-capped with compounds which will provide the required terminal groupings on the polymer and provided the polymer or its precursors and/or intermediates is/are diluted in the inert fluid described above during the polymerisation process. Preferred routes to the preparation of said polymers include

(i) polycondensation
(ii) ring opening/equilibrium

(iii) polyaddition
(iv) chain extension

[0045] (i) Polycondensation (i.e. the polymerisation of multiple monomers and/or oligomers with the elimination of low molecular weight by-product(s) such as water, ammonia or methanol etc.).
Any suitable polycondensation reaction pathway may be utilised. Preferred are polycondensation reactions relying on the reaction schemes below:-

[0046] The sort of reaction envisaged between the condensable end groups of the starting materials are most preferably generally linked to the interaction of compounds having hydroxyl and/or hydrolysable end groups which can interact with the release of e.g. water or methanol or the like. However, the following list indicates other interactions which might be considered for the cure process of the composition in accordance with the present invention:-

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,
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.

[0047] Most preferably the condensation reaction which occurs between monomers/oligomers and intermediates with hydroxyl and/or alkoxy end-groups thereby producing water or alcohols as a by-product.

[0048] A preferred method for the polymerisation process is the polymerisation of straight chain precursors and/or branched organopolysiloxanes of formula (1) including for example

$$R_{(3-f)}R^5{}_fSiO(R_2SiO)_gSiR_{(3-f)}R^5{}_f$$

$$R_{(3-f)}R^5{}_fSiO(RR^1SiO)_hSiR_{(3-f)}R^5{}_f$$

$$R_{(3-f)}R^5{}_fSiO[(R_2SiO)_j(RR^5SiO)_k]SiR_{(3-f)}R^5{}_f$$

Where R is as previously defined, R^5 is –OH or an alkoxy group having from 1 to 6 carbon atoms, preferably a methoxy or ethoxy group, f is 0 or 1, preferably 1, g is an integer from 2 to 100, h is from 2 to 100, j is an integer from1 to 100 and k is an integer between 1 to 100. Some branching may occur with the presence of other groups in the polymeric chain but preferably this is kept to a minimum.

[0049] The above starting materials preferably have a viscosity of between 10mPa.s and 5000mPa.s at 25°C.

[0050] Many of the above processes require the presence of catalyst. Any suitable polycondensation catalyst may be utilised including 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.

[0051] Tin catalysts may include 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 bisneodecanoate Dibutyltin dibenzoate, stannous octoate, dimethyltin dineodeconoate, dibutyltin dioctoate. Dibutyltin dilaurate, dibutyltin diacetate are particularly preferred.

[0052] Titanate catalysts may comprise a compound according to the general formula $Ti[OR^{20}]_4$ and $Zr[OR^{20}]_4$ respectively where each R^{20} 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^{20} 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^{20} is the same, R^{20} is an isopropyl, branched secondary alkyl group or a tertiary alkyl group, in particular, tertiary butyl. Examples include tetrabutyltitanate, tetraisopropyltitanate, or chelated titanates or zirconates such as for example diisopropyl bis(acetylacetonyl)titanate, diisopropyl bis(ethylacetoacetonyl)titanate, diisopropoxytitanium Bis(Ethylacetoacetate) and the like. Further examples of suitable catalysts are described in EP1254192 and/or WO200149774 the contents of which are incorporated herein by reference. The amount of catalyst used depends on the cure system being used but typically is from 0.01 to 3% by weight of the total composition.

[0053] Other condensation catalysts which may be used, 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 $FeCl_3$, $AlCl_3$, $ZnCl_2$, and $ZnBr_2$.

[0054] More preferred are condensation specific catalysts such as acidic condensation catalysts of the formula $R^{21}SO_3H$ in which R^{21} represents an alkyl group 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^{21} 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-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 US3839388, US4564693 or EP215470 and phosphonitrile halide ion based catalysts, as described in GB2252975, having the general formula $[X(PX_2{=}N)_pPX_3]^+[M^2X_{(m-n+1)}R^{III}{}_m]^-$, wherein X 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, p has a value of from 1 to 6, m is the valence or oxidation state of M^2 and n has a value of from 0 to m-1.

[0055] Alternatively the catalyst may comprise an oxygen-containing chlorophosphazene containing organosilicon radicals having the following general formula:-

$$Z^1\text{-}PCl_2{=}N(\text{-}PCl_2{=}N)_q\text{–}PCl_2\text{-}O$$

in which

Z^1 represents an organosilicon radical bonded to phosphorus via oxygen, a chlorine atom or the hydroxyl group and

q 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).

[0056] 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.

[0057] 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 such as an amine such as a mono/di and trialkanolamines for example monoethanolamine (MEA) and triethanolamine (TEA). 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 when the desired viscosity has been reached, the viscosity of the organosilicon compound obtained in the process can be kept constant by a procedure in which the catalyst used, or a reaction product which has been formed from this catalyst by reaction with organosilicon compound to be subjected to condensation and/or equilibration and likewise promotes the condensation and/or equilibration of organosilicon compounds, is inhibited or deactivated by addition of inhibitors or deactivators which have been employed to date in connection with phosphazenes, for example, triisononylamine, n-butyllithium, lithium siloxanolate, hexamethylcyclotrisilazane, hexamethyldisilazane and magnesium oxide.

[0058] Where required the polymer obtained may be end-blocked as a means of regulating the molecular weight of the polymer and/or to add functionality. Whilst this end-blocking function can be achieved by water as discussed above, other suitable end-blocking agents include silanes having 1 group capable of reacting with the terminal groups of the resulting polymeric constituent prepared in the diluted polymer to produce the required end-groups for polymer (a).

(III) POLYADDITION

[0059] For the sake of this specification a "polyaddition" or "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 monomeric and oligomeric co-reactants during polymerisation. A preferred addition polymerisation route is a hydrosilylation reaction between an unsaturated organic group e.g. an alkenyl or alkynyl group and an Si-H group in the presence of a suitable catalyst. In this route suitable silanes may be utilised as well as siloxane containing monomers and/or oligomers.

[0060] Typically the polyaddition route is utilised to form block copolymers by reacting
a) (i) an organopolysiloxane or (ii) a silane with:-
b) one or more organopolysiloxane polymer(s)

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

[0061] The organopolysiloxane or silane (a) is selected from a silane (a) (ii) containing at least one group capable of undergoing addition type reactions and an organopolysiloxane monomer (a) (i) containing groups capable of undergoing addition type reactions. The organopolysiloxane or silane (a) must contain substituents such that it is capable of undergoing an appropriate addition reaction with polymer (b). The preferred addition reaction is a hydrosilylation reaction between an unsaturated group and an Si-H group.

[0062] Preferably silane (a) (ii) has at least 1 and preferably 2 groups capable of undergoing addition type reactions with (b). When the addition reaction is a hydrosilylation reaction the silane may contain an unsaturated constituent but preferably contains at least one Si-H group.

Most preferably each silane contains one or more Si-H groups. In addition to the one or more Si-H groups, preferred silanes may include for example an alkyl group, an alkoxy group, an acyloxy group, a ketoximato group, an amino group, an amido group, an acid amido group, an aminoxy group, a mercapto group, an alkenyloxy group and the like. Among these, alkoxy, acyloxy, ketoximato, amino, amido, aminoxy, mercapto and alkenyloxy groups are preferred. Practical examples of the silicon hydride are halosilane tri-chlorosilane, methyl dichlorosilane, dimethyl chlorosilane, and phenyl dichlorosilane; alkoxy silanes, such as tri-methyoxy silane, tri-ethoxy silane, methyl di-ethoxy silane, methyl di-methoxy silane and phenyl-di-methoxy silane; acyloxy silanes, such as methyl di-acetoxy silane and phenyl diacetoxy silane; and ketoximato silanes, such as bis-(dimethyl-ketoximate)-methyl silane and bis-(cyclohexyl ketoximate)methyl silane. Among them, halosilanes and alkoxyl silanes are preferred. Particularly preferred silanes include for example methyl dimethoxy silane (H-Si $(-CH_3)$ $(-OCH_3)_2$).

[0063] It will be appreciated that the addition reaction between silane (a) (ii) and (b) results in a polymer chain extension process or as a means of end - blocking a polymer with pre-required end groups, in which case the extender may be added in combination with silane (a) (ii), i.e. immediately prior to the addition reaction or may be present during the polymerisation of polymer (b) and as such silane (a) (ii) is added to an extended polymer (b) which has been polymerised in the presence of the extender.

[0064] Organopolysiloxane monomer (a) (i) is preferably in the form of a straight chain and/or branched organopolysiloxane comprising units of formula (1a)

$$R'_{a'}SiO_{4-a'/2} \qquad (1a)$$

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 a' has, on average, a value of from 1 to 3, preferably 1.8 to 2.2. Preferably each R' is the same or different and is exemplified by, but not limited to hydrogen, 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. Some R' groups may be hydrogen groups. Preferably the polydiorganosiloxanes are polydialkylsiloxanes, most preferably polydimethylsiloxanes. When (a) 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 (b) via an addition reaction process. Preferably organopolysiloxane (a) (i) comprises at least one Si-H per molecule, preferably at least two Si-H groups per molecule. Preferably organopolysiloxane (a) (i) is end-blocked with a siloxane group of the formula $H(R")_2SiO_{1/2}$, wherein each R" is a hydrocarbon or substituted hydrocarbon group, most preferably an alkyl group. Preferably organopolysiloxane (a) (i) has a viscosity of between 10mPa.s and 5000mPa.s at 25°C.

[0065] Organopolysiloxane polymer (b) is preferably a straight chain and/or branched organopolysiloxane comprising units of formula (1b)

$$R'''_{a'}SiO_{4-a'/2} \qquad (1b)$$

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 a' is as previously described. Preferably 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.

[0066] Organopolysiloxane polymer (b) may comprise any suitable organopolysiloxane polymeric backbone but is preferably linear or branched, and comprises at least one, preferably at least two substituent groups which will react with the aforementioned groups in the organopolysiloxane or silane (a) via an addition reaction pathway., Preferably the or each addition reactive substituent group of polymer (b) is a terminal group. When the organopolysiloxane or silane (a) comprises at least one Si-H group, the preferred substituent groups on organopolysiloxane polymer (b), 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 ($CH_2=CHCH_2$-)) or terminated with acrylic or alkylacrylic such as $CH_2=C(CH_3)-CH_2$- groups Representative, non- limiting examples of the alkenyl groups are shown by the following structures; $H_2C=CH$-, $H_2C=CHCH_2$-, $H_2C=C(CH_3)CH_2$- , $H_2C=CHCH_2CH_2$-, $H_2C=CHCH_2CH_2CH_2$-, and $H_2C=CHCH_2CH_2CH_2CH_2$-

. Representative, non- limiting examples of alkynyl groups are shown by the following structures; HC≡C-, HC≡CCH$_2$-, HC≡CC(CH$_3$) - , HC≡CC(CH$_3$)$_2$ - , HC≡CC(CH$_3$)$_2$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.

[0067] In cases where the organopolysiloxane or silane (a) comprises only one addition reactable group and (b) comprises two addition reactable groups which will react with the organopolysiloxane or silane (a), the resulting product will be an "ABA" type polymeric product. Whereas when both the organopolysiloxane or silane (a) comprises two addition reactable groups and (b) comprises two addition reactable groups which will react with the organopolysiloxane or silane (a) interaction between the two components would lead to (AB)n block copolymers in which the length of the polymer is largely determined by the relative amounts of the two constituents.

[0068] It will also be appreciated that this hydrosilylation route may be utilised to prepare silicone-organic copolymers by using an organopolysiloxane polymer which contains organic groups in the polymer backbone or by replacing organopolysiloxane polymer (b) with, for example, alkenyl terminated polyethers. Hence linear non-hydrolysable (AB)n block copolymers in accordance with the present invention can be prepared by catalyzed hydrosilylation 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 and/or hydrogen (dialkyl) siloxy groups (dependent on the relative amounts of the constituents which are present).

[0069] 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 hydrocarbon group on the polyoxyethylene. The metals are illustrated by ruthenium, rhodium, palladium, osmium, iridium, or platinum.

[0070] Hydrosilylation catalysts are illustrated by the following; chloroplatinic acid, alcohol modified chloroplatinic acids, olefin complexes of chloroplatinic acid, complexes of chloroplatinic acid and divinyltetramethyldisiloxane, fine platinum particles adsorbed on carbon carriers, platinum supported on metal oxide carriers such as $Pt(Al_2O_3)$, platinum black, platinum acetylacetonate, platinum(divinyltetramethyldisiloxane), platinous halides exemplified by $PtCl_2$, $PtCl_4$, $Pt(CN)_2$, complexes of platinous halides with unsaturated compounds 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 platinous chloride and divinyl tetramethyl disiloxane, for example as described in US Patent 5,175,325.

[0071] Ruthenium catalysts such as $RhCl_3(Bu_2S)_3$ and ruthenium carbonyl compounds such as ruthenium 1,1,1-trifluoroacetylacetonate, ruthenium acetylacetonate and triruthinium dodecacarbonyl or a ruthenium 1,3-ketoenolate may alternatively be used.

[0072] Other hydrosilylation catalysts suitable for use in the present invention include for example rhodium catalysts such as $[Rh(O_2CCH_3)_2]_2$, $Rh(O_2CCH_3)_3$, $Rh_2(C_8H_{15}O_2)_4$, $Rh(C_5H_7O_2)_3$, $Rh(C_5H_7O_2)(CO)_2$, $Rh(CO)[Ph_3P](C_5H_7O_2)$, $RhX^4_3[(R^3)_2S]_3$, $(R^2_3P)_2Rh(CO)X^4$, $(R^2_3P)_2Rh(CO)H$, $Rh_2X^4_2Y^4_4$, $H_aRh_bolefin_cCl_d$, $Rh\ (O(CO)R^3)_{3-n}(OH)_n$ 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^3 is an alkyl radical, cycloalkyl radical or aryl radical and R^2 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 $Ir(OOCCH_3)_3$, $Ir(C_5H_7O_2)_3$, $[Ir(Z^2)(En)_2]_2$, or $(Ir(Z^2)(Dien)]_2$, where Z^2 is chlorine, bromine, iodine, or alkoxy, En is an olefin and Dien is cyclooctadiene may also be used.

[0073] 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.

[0074] Typically when (a) has at least two Si-H groups, typically, the process is carried out using approximately a 1:1 molar ratio of (a) to (b). However, useful materials may also be prepared by carrying out the process with an excess of either (a) or (b) but this would be considered a less efficient use of the materials. Typically, the material containing the unsaturation (b) is used in slight excess to ensure all the Si-H is consumed in the reaction. As polymer (b) used in the present invention is preferably terminated with unsaturated end-groups, end-blocking agents are not typically required when making the polymer via this route. However, they may be utilised if required.

[0075] Optionally when a hydrosilylation route is utilised for polymerisation 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 polymethylvinylcyclosiloxanes having three to six methylvinylsiloxane units per molecule.

[0076] Compositions containing these hydrosilylation catalysts typically require heating at temperatures of 70°C or above to cure at a practical rate, particularly if an inhibitor is used. Room temperature cure is typically accomplished with such systems by use of a two-part system in which the cross-linker and inhibitor are in one of the two parts and the platinum is in the other part. The amount of platinum is increased to allow for curing at room temperature. The optimum concentration of platinum catalyst inhibitor is that which will provide the desired storage stability or pot life at ambient temperature without excessively prolonging the time interval required to cure the present compositions at elevated temperatures. This amount will vary widely and will depend upon the particular inhibitor that is used. Inhibitor concentrations as low as one mole of inhibitor per mole of platinum will in some instances yield a desirable level of storage stability and a sufficiently short curing period at temperatures above about 70° C. In other cases, inhibitor concentrations of up to 10, 50, 100, 500 or more moles per mole of platinum may be needed. The optimum concentration for a particular inhibitor in a given composition can be determined by routine experimentation.

[0077] 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 based catalysts.

[0078] For this type of polymerisation the amount of hydrosilylation catalyst used is not narrowly limited as long as there is a sufficient amount to accelerate a reaction between

(a) (i) an organopolysiloxane or (ii) a silane the chosen of which must contain at least one and preferably at least two Si-H groups with

(b) one or more organopolysiloxane polymer(s) or an alternative therefore such as a polyoxyethylene having an unsaturated hydrocarbon group at each molecular terminal at room temperature or at temperatures above room temperature. The actual 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 (a) and (b). The catalyst can be added at an amount 10 to 120 weight parts per one million parts of components (a) and (b), but is typically added in an amount from 10 to 60 weight parts per one million parts of (a) and (b).

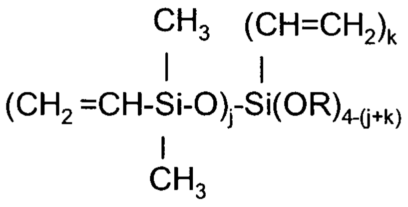
[0079] Where appropriate, polymers obtained via a hydrosilylation route can also be cured and/or crosslinked by a hydrosilylation reaction catalyst in combination with an organohydrogensiloxane as the curing agent providing each polymer molecule produced contains at least two unsaturated groups suitable for cross-linking with the organohydrogensiloxane. To effect curing of the present composition, the organohydrogensiloxane 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 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.

(IV) CHAIN EXTENSION

[0080] 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. 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 as hereinbefore described.

[0081] For pre-formed polymers with alkenyl or Si-H groups (typically end groups) suitable for addition reactions via a hydrosilylation route the chain extender will contain two groups which will undergo an addition reaction with the respective addition reactive groups on the chosen polymer. Such chain extenders may 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



$$(\mathrm{CH_2{=}CH{-}}\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{CH_3}}{\mathrm{Si}}}\mathrm{{-}O})_j{-}\overset{(\mathrm{CH{=}CH_2})_k}{\mathrm{Si}}(\mathrm{OR})_{4-(j+k)}$$

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, $(\mathrm{ViMe_2SiO})_2\mathrm{SiVi(OMe)}_1$ $(\mathrm{ViMe_2SiO})_1\mathrm{SiVi(OMe)}_2$, $(\mathrm{ViMe_2SiO})_2\mathrm{SiVi(OEt)}_1$, $(\mathrm{ViMe_2SiO})_1\mathrm{SiVi(OEt)}_2$, $(\mathrm{ViMe_2SiO})_3\mathrm{Si(OMe)}_1$, $(\mathrm{ViMe_2SiO})_2\mathrm{Si(OMe)}_2$, $(\mathrm{ViMe_2SiO})_3\mathrm{Si(OEt)}_1$ and $(\mathrm{ViMe_2SiO})_2\mathrm{Si(OEt)}_2$

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

[0082] 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.

[0083] 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.

[0084] 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.

[0085] 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. 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 methyltrimethoxysilane (where appropriate) or by physical separation using evaporation, coalescing or centrifuging techniques.

[0086] The process can be carried out either batchwise or continuously on any suitable mixers. In case of a polycondensation, generated water may, if required, be removed by chemical drying using e.g. hydrolysable silanes like methyltrimethoxysilane or by physical separation using evaporation, coalescing or centrifuging techniques.

[0087] The Hydrophobic fillers of step (iii) in accordance with the method of the present invention for the preparation of foam control agents are well known and may be materials such as silica, preferably with a surface area as measured by BET measurement of at least 50 m²/g, titania, ground quartz, alumina, an aluminosilicate, an organic waxes e.g. polyethylene wax or microcrystalline wax, zinc oxide, magnesium oxide, a salt of an aliphatic carboxylic acids, a reaction product of an isocyanate with an amine, e.g. cyclohexylamine, or an alkyl amide such as ethylenebisstearamide or methylenebisstearamide. Mixtures of two or more of these can be used. Silica fillers are particularly preferred. Preferred silica materials are those which are prepared by heating, e.g. fumed silica, or precipitation, although other types of silica such as those made by gel formation are also acceptable. The silica filler may for example have an average particle size of 0.5 to 50μm, preferably 2 to 30 and most preferably 5 to 25μm. Such materials are well known and are commercially available, both in hydrophilic form and in hydrophobic form.

[0088] Some of the fillers mentioned above are not hydrophobic in nature, but can be used if made hydrophobic. Such fillers may be rendered hydrophobic either in situ (i.e. by introducing a hydrophobing agent before during or after step (iii) of the process of the present invention, or by pre-treatment of the filler prior to step (iii) of the process. The hydrophobing of fillers, where required may be carried out by treatment with a fatty acid, but is preferably done by the use of methyl substituted organosilicon materials. Suitable hydrophobing agents include polydimethylsiloxanes, dimethylsiloxane polymers which are end-blocked with silanol or silicon-bonded alkoxy groups, hexamethyldisilazane, hexamethyldisiloxane. The organosilicon resins optionally introduced in step (iv) of the process in accordance with the invention (as discussed below) may also function as filler hydrophobing agents.

[0089] The amount of filler in the foam control agent of the invention is preferably from 0.5 to 50% by weight based on polysiloxane containing polymer, more preferably from 1 up to 10 or 15% and most preferably 2 to 8%. When present, it is also preferred that the ratio of the weight of organosilicon resin to filler is from 1/10 to 20/1, preferably 1/5 to 10/1, most preferably 1/2 to 6/1.

[0090] Where the filler needs to be made hydrophobic in situ, the manufacturing process would include a heating stage, preferably under reduced pressure, in which the filler and the treating agent are mixed together in part or all of polysiloxane containing polymer and/or all or part of fluid (B), possibly in the presence of a suitable catalyst, where required.

[0091] The optional organosilicon resin which may be introduced in accordance with step (iv) of the present invention is generally a non-linear siloxane resin and comprises (and most preferably consists of) siloxane units of the formula $R^{25}{}_sSiO_{4-s/2}$ wherein R^{25} denotes a hydroxyl, hydrocarbon or hydrocarbonoxy group, and wherein *s* has an average value of from 0.5 to 2.4. It preferably consists of monovalent trihydrocarbonsiloxy (M) groups of the formula $R^{26}{}_3SiO_{1/2}$ and tetrafunctional (Q) groups $SiO_{4/2}$ wherein R^{26} denotes a monovalent hydrocarbon group. The number ratio of M groups to Q groups is preferably in the range 0.4:1 to 2.5:1 (equivalent to a value of a in the formula $R^{25'}{}_sSiO_{4-s/2}$ of 0.86 to 2.15), more preferably 0.4:1 to 1.1:1 and most preferably 0.5:1 to 0.8:1 (equivalent to s=1.0 to s=1.33). The organosilicon resin is preferably a solid at room temperature but MQ resins having a M/Q ratio higher than 1.2, which are generally liquids, can be used successfully. For industrial foam control applications such as defoaming of black liquor in the paper and pulp industry, resins having a high M/Q ratio may be preferred. Although it is most preferred that the resin consists only of monovalent and tetravalent siloxy units as defined above, a resin comprising M groups, trivalent $R^{25}SiO_{3/2}$ (T) units and Q units can alternatively be used. It is also acceptable that up to 20% of all units present can be divalent units $R^{25}{}_2SiO_{2/2}$. The group R^{25} is preferably an alkyl group having 1 to 6 carbon atoms, for example methyl or ethyl, or can be phenyl. It is particularly preferred that at least 80%, most preferably substantially all, R^{25} groups present are methyl groups. Other hydrocarbon groups may be present, e.g. alkenyl groups present for example as dimethylvinylsilyl units, preferably not exceeding 5% of all R^{25} groups. Silicon bonded hydroxyl groups and/or alkoxy, e.g. methoxy groups may also be present.

[0092] Such organosilicon resins are well known. They can be made in solvent or in situ, e.g. by hydrolysis of certain silane materials. Particularly preferred is the hydrolysis and condensation in the presence of a solvent e.g. xylene of a precursor of the tetravalent siloxy unit (e.g. tetraorthosilicate, tetraethyl orthosilicate, polyethyl silicate or sodium silicate) and a precursor of monovalent trialkylsiloxy units (e.g. trimethylchlorosilane, trimethylethoxysilane, hexamethyldisiloxane or hexamethyldisilazane). The resulting MQ resin can if desired be further trimethylsilylated to react out residual Si-OH groups or can be heated in the presence of a base to cause self-condensation of the resin by elimination of Si-OH groups.

[0093] When present the organosilicon resin is preferably present in the antifoam at from 0.1 to 20% by weight of the formulation, and most preferably from 0.5 to 10%.

[0094] The organosilicon resin may be insoluble in the inert organopolysiloxane but is generally insoluble in the organic fluid but may be soluble or insoluble in the polysiloxane containing polymer and may be soluble or insoluble in the mixture of step (i) of the process in accordance with the present invention.

[0095] In step (iv) of the process in accordance with the present invention the resin can be added into the foam control agent as a solution in a non-volatile solvent, for example an alcohol such as dodecanol or 2-butyl-octanol or an ester such as octyl stearate. A resin solution prepared in a volatile solvent such as xylene can be mixed with the non-volatile solvent and the volatile solvent removed by stripping or other form of separation. In most cases the non-volatile solvent can be left in the foam control agent. It is preferred that the resin is dissolved in an equal amount of non-volatile solvent or less, preferably no more than half its weight of solvent. If the resin is added as a solution and is insoluble in the mixture of polysiloxane containing polymer and organic liquid, it will generally form solid particles of acceptable particle size on mixing.

[0096] The resin can alternatively be added into the foam control agent in the form of solid particles, for example spray dried particles or flakes etc.. Spray dried MQ resins are available commercially, for example of average particle size 10 to 200 microns.

[0097] When required in a composition prepared by the method in accordance with the present invention the means by which organosilicon resin is introduced during step (iv) may be dependent on solubility of the resin. Solubility can be measured by observing a mixture of the resin of step (iv) in accordance with the invention with the polysiloxane containing and/or its precursors and/or the inert organopolysiloxane and/or organic fluid using an optical microscope.

[0098] The factors affecting the solubility of the resin in the mixture in step (i) of the process in accordance with the present invention include the chemical nature of the starting materials and of the resulting polymer produced.

[0099] The level of insolubility of the resin in the mixture of polysiloxane containing polymer and liquid (B) may affect its particle size in the composition. The lower the solubility of the siloxane resins in the constituents of step (i) of the process in accordance with the present invention the larger the particle size tends to be when the resin is introduced in step (iv). Thus a siloxane resin which is soluble at 1% by weight in the constituents of step (i) of the process in accordance with the present invention will tend to form smaller particles than a resin which is only soluble at 0.01% by weight. Resins which are partly soluble in the mixture of step (i), that is having a solubility of at least 0.1% by weight, are preferred.

[0100] The molecular weight of the resin can be increased by condensation, for example by heating in the presence of a base. The base can for example be an aqueous or alcoholic solution of potassium hydroxide or sodium hydroxide, e.g. a solution in methanol or propanol. The MQ resins of increased molecular weight have improved resistance to loss of performance over time when stored in contact with the detergent, for example as an emulsion in liquid detergent. The reaction between resin and base may be carried out in the presence of the silica, in which case there may be some reaction between the resin and the silica. The reaction with base can be carried out in the presence of the polysiloxane containing polymer and/or in the presence of the non-volatile solvent and/or in the presence of a volatile solvent. The reaction with base may hydrolyse an ester non-volatile solvent such as octyl stearate but we have found that this does not detract from the foam control performance.

[0101] The foam control agents according to the present invention may be provided as a product of the process in accordance with the present invention, but for some applications it may be preferred to make them available in alternative forms. For example for use in aqueous media, it may be appropriate to provide the foam control agent in an emulsion form, preferably an oil-in-water emulsion.

[0102] Preferably the viscosity of the mixture of the polymer and inert fluid prior to emulsifying is in the range of viscosity of from 500 to 10 000 000 mPa.s at 25°C most preferably 1000 to 100 000 mPa.s at 25°C.

[0103] Methods of providing silicone-based foam control agents in oil-in-water emulsion form are known and have been described in a number of publications and patent specifications. Examples are EP913187, EP978628, WO9822196, WO9800216, GB2315757, EP499304 and EP459512. Emulsions may be made according to any of the known techniques, and may be macro-emulsions or micro-emulsions, however macro-emulsions are preferred.

[0104] In general, they comprise the foam control agent as the disperse phase, one or more surfactants, water and standard additives, such as preservatives, viscosity modifiers and thickeners. The surfactants may be selected from anionic, cationic, nonionic or amphoteric materials. Mixtures of one or more of these may also be used.

[0105] Any suitable surfactant or combination of surfactants may be utilised. The surfactant can in general be a non-ionic surfactant, a cationic surfactant, an anionic surfactant, or an amphoteric surfactant, although not all procedures for carrying out the process of the invention can be used with all surfactants. The amount of surfactant used will vary depending on the surfactant, but generally is up to about 30 wt. % based on the polydiorganosiloxane.

[0106] Examples of nonionic surfactants include condensates of ethylene oxide with long chain fatty alcohols or fatty acids such as a C_{12-16} alcohol, condensates of ethylene oxide with an amine or an amide, condensation products of ethylene and propylene oxide, esters of glycerol, sucrose, sorbitol, fatty acid alkylol amides, sucrose esters, fluoro-surfactants, fatty amine oxides, polyoxyalkylene alkyl ethers such as polyethylene glycol long chain (12-14C) alkyl ether, polyoxyalkylene sorbitan ethers, polyoxyalkylene alkoxylate esters, polyoxyalkylene alkylphenol ethers, ethylene glycol propylene glycol copolymers and alkylpolysaccharides, for example materials of the structure R^{24}-O-(R^{25}O)$_s$-(G)$_t$ wherein R^{24} represents a linear or branched alkyl group, a linear or branched alkenyl group or an alkylphenyl group, R^{25} represent an alkylene group, G represents a reduced sugar, s denotes 0 or a positive integer and t represent a positive integer as described in US Patent 5,035,832. non ionic surfactants additionally include polymeric surfactants such as polyvinyl alcohol (PVA) and polyvinylmethylether. Suitable nonionic surfactants include silicones such as those described as Surfactants 1 to 6 in EP 638346, particularly siloxane polyoxyalkylene copolymers, condensates of ethylene oxide with a long chain (fatty) alcohol or (fatty) acid, for example C_{14-15} alcohol, condensed with 7 moles of ethylene oxide (Dobanol® 45-7), condensates of ethylene oxide with an amine or an amide, condensation products of ethylene and propylene oxides, fatty acid alkylol amides, fatty amine oxides, esters of sucrose, glycerol or sorbitol and fluoro-surfactants

[0107] Representative examples of suitable commercially available nonionic surfactants include polyoxyethylene fatty alcohols sold under the tradename BRIJ® by Uniqema (ICI Surfactants), Wilmington, Delaware and. Some examples are BRIJ® 35 Liquid, an ethoxylated alcohol known as polyoxyethylene (23) lauryl ether, and BRIJ® 30, another ethoxylated alcohol known as polyoxyethylene (4) lauryl ether. polyoxyethylene fatty alcohols sold under the tradename VOLPO® by Croda NV; ethoxylated alcohols sold under the trademark TERGITOL® by The Dow Chemical Company, Midland, Michigan. Some example are TERGITOL® TMN-6, an ethoxylated alcohol known as ethoxylated trimethylnonanol; and various of the ethoxylated alcohols, i.e., C_{12}-C_{14} secondary alcohol ethoxylates, sold under the trademarks TERGITOL® 15-S-5, TERGITOL® 15-S-12, TERGITOL® 15-S-15, and TERGITOL® 15-S-40. Surfactants containing silicon atoms can also be used.

[0108] Examples of suitable amphoteric surfactants include imidazoline compounds, alkylaminoacid salts, and betaines. Specific examples include cocamidopropyl betaine, cocamidopropyl hydroxysulfate, cocobetaine, sodium cocoamidoacetate, cocodimethyl betaine, N-coco-3-aminobutyric acid and imidazolinium carboxyl compounds. Suitable amphoteric organic detergent surfactants include imidazoline compounds, alkylaminoacid salts and betaines Representative examples of suitable amphoteric surfactants include imidazoline compounds, alkylaminoacid salts, and betaines.

[0109] Examples of cationic surfactants include quaternary ammonium hydroxides such as octyl trimethyl ammonium hydroxide, dodecyl trimethyl ammonium hydroxide, hexadecyl trimethyl ammonium hydroxide, octyl dimethyl benzyl ammonium hydroxide, decyl dimethyl benzyl ammonium hydroxide, didodecyl dimethyl ammonium hydroxide, dioctadecyl dimethyl ammonium hydroxide, tallow trimethyl ammonium hydroxide and coco trimethyl ammonium hydroxide as well as corresponding salts of these materials, Suitable cationic organic surfactants include alkylamine salts, quaternary ammonium salts, sulphonium salts and phosphonium salts.fatty amines and fatty acid amides and their derivatives, basic pyridinium compounds, quaternary ammonium bases of benzimidazolines and polypropanolpolyethanol amines. Other representative examples of suitable cationic surfactants include alkylamine salts, sulphonium salts, and phosphonium salts.

[0110] Examples of suitable anionic surfactants include alkyl sulphates such as lauryl sulphate, polymers such as acrylates/C_{10-30} alkyl acrylate crosspolymer alkylbenzenesulfonic acids and salts such as hexylbenzenesulfonic acid, octylbenzenesulfonic acid, decylbenzenesulfonic acid, dodecylbenzenesulfonic acid, cetylbenzenesulfonic acid and myristylbenzenesulfonic acid; the sulphate esters of monoalkyl polyoxyethylene ethers; alkylnapthylsulfonic acid; alkali metal sulforecinates, sulfonated glyceryl esters of fatty acids such as sulfonated monoglycerides of coconut oil acids, salts of sulfonated monovalent alcohol esters, amides of amino sulfonic acids, sulfonated products of fatty acid nitriles, sulfonated aromatic hydrocarbons, condensation products of naphthalene sulfonic acids with formaldehyde, sodium octahydroanthracene sulfonate, alkali metal alkyl sulphates, ester sulphates, and alkarylsulfonates. Suitable anionic organic surfactants include alkali metal soaps of higher fatty acids, alkyl aryl sulphonates, for example sodium dodecyl benzene sulphonate, long chain (fatty) alcohol sulphates, olefin sulphates and sulphonates, sulphated monoglycerides, sulphated esters, sulphonated or sulphated ethoxylate alcohols, sulphosuccinates, alkane sulphonates, phosphate esters, alkyl isethionates, alkyl taurates and/or alkyl sarcosinates.Anionic surfactants include alkali metal soaps of higher fatty acids, alkylaryl sulphonates such as sodium dodecyl benzene sulphonate, long chain fatty alcohol sulphates, olefin sulphates and olefin sulphonates, sulphated monoglycerides, sulphated esters, sulphonated ethoxylated alcohols, sulphosuccinates, alkane sulphonates, phosphate esters, alkyl isethionates, alkyl taurates, and alkyl sarcosinates. One example of a preferred anionic surfactant is sold commercially under the name Bio-Soft N-300. It is a triethanolamine linear alkylate sulphonate composition marketed by the Stephan Company, Northfield, Illinois.

[0111] The above surfactants may be used individually or in combination.

[0112] In a preferred embodiment of the present invention the polymerisation catalyst is selected with a view to additionally being the or one of the surfactants involved in the emulsification process. A particularly preferred family of catalysts which also function as surfactants when present in antifoam compositions are acidic condensation catalysts such as for example DBSA as discussed above.

[0113] Nonionic or anionic surfactants are preferred. Of particular interest are surfactants which are environmentally acceptable. The concentration of foam control agent in an emulsion may vary according to applications, required viscosity, effectiveness of the foam control agent and addition system, and ranges on average from 5 to 80% by weight, preferably 10 to 50%, more preferably 25 to 40%.

[0114] A foam control emulsion may also contain a stabilising agent such as a silicone glycol copolymer or a crosslinked organopolysiloxane polymer having at least one polyoxyalkylene group as described in EP 663225.

[0115] Phase inversions generally occurs when the continuous phase of a dispersion becomes the dispersed phase, or vice versa. Phase inversions in liquid/liquid dispersions generally are known in the art to be effected by one of two methods. An inversion may be caused by changing the phase ratio until there is a high enough ratio of the dispersed phase that it becomes the continuous phase. Alternatively, a transitional inversions may occur when the affinity of the surfactant for the two phases is altered in order to cause the inversion. Typically, the inversions occurring in this invention occur due to a change in the phase ratio.

[0116] Thus, the inversion method used to make emulsions, according to the invention, is carried out by forming an oil phase containing the diluted polysiloxane containing polymer and mixing and agitating the oil phase. A limited and very small amount of water is added to the oil phase in a stepwise fashion, such that an inversion occurs, and an oil-in-water emulsion is formed. Generally, the amount of water required is about 0.5 to 10 percent by weight based on the cumulative weight of polysiloxane containing polymer present in the oil phase. Preferably, the amount of water will be about 1 to 5 percent by weight based on the weight of the polysiloxane containing polymer present in the oil phase. While the water can be added in 2 to 4 portions, addition of water in a single portion is preferred. The initial addition of water can include the surfactant. After the desired particle size has been reached, the emulsion is diluted with the balance of water to achieve the preferred solids content.

[0117] The emulsions produced by the process of this invention can have a wide variety of polysiloxane containing polymer concentrations, particle sizes and molecular weights, including novel materials having high concentrations of large particle polysiloxane containing polymer of high molecular weight. The particle size can for example be chosen within the range 0.1 to 1000 micrometres.

[0118] The quantity of water and/or surfactant used in the initial phase inversion process may have an impact on the particle size of the final emulsion. For instance, if an emulsion is formed with the same quantity of water in two instances but in the first a large quantity of water is mixed before the phase inversion step and in the second a small quantity of water is mixed before the phase inversion step followed by mixing the remaining additional water after the phase inversion step, the first emulsion will generally have a larger particle size than the second. No matter how the water is added, the total amount of water used is generally between about 1 and 99 wt. %, preferably between about 6 and about 99 wt. %, based on the weight of the emulsion.

[0119] If desired, other materials can be added to either phase of the emulsions, for example, colorants, thickeners, preservatives, freeze thaw stabilizer, inorganic salts to buffer pH, or active ingredients such as pharmaceuticals.

[0120] Alternatively the foam control agent can be provided as a water-dispersible composition in which the product resulting from the process in accordance with the present invention is dispersed in a water-dispersible component such as a silicone glycol or in another water-miscible liquid such as ethylene glycol, propylene glycol, polypropylene glycol, polyethylene glycol, a copolymer of ethylene glycol and propylene glycol, an alkyl polyglycoside, an alcohol alkoxylate or an alkylphenol alkoxylate.

[0121] An alternative form of providing a foam control agent according to the present invention is in powdered or granulated form. This is particularly useful when the agent is to be used in a powdered product, e.g. a detergent powder. Any suitable method for the production of powdered or granulated foam control agents may be used with foam control agents produced using the method of the present invention. Granulated foam control agents may, for example, be made by a variety of methods, including granulators, spray drying, emulsification followed by drying, spray mixing, spray chilling, compactors, extruders, high shear mixing, low shear mixing and flaking. Such methods have been extensively described in the patent literature and these are exemplified by an extensive list of publications in US6521587.

[0122] Suggested ingredients of particulate foam control agents include, in addition to the foam control agent itself, a binder or encapsulant and a carrier or support for the granule. It is preferred that any carrier or binder material should contribute to the efficiency or activity of the product in which it is to be incorporated. A surfactant may be used to aid dispersion of the silicone and organic liquid in the encapsulant or binder. Sometimes other ingredients are incorporated, for example dyes, pigments, preservatives or materials to aid the dispersion in the aqueous medium in which the foam control agent is supposed to be active such as the surfactants described above in connection with foam control emulsions. Such a surfactant may help in controlling the "foam profile", that is in ensuring that some foam is visible throughout the wash without overfoaming.

[0123] Binders and/or encapsulants used in particulate foam control agents may comprise waxes and/or aqueous film forming polymers. Examples include dextrine, polypeptides, polyoxyalkylene polymers such as polyethylene glycol, which can be applied molten or as an aqueous solution and spray dried, reaction products of tallow alcohol and ethylene oxide, or polypropylene glycol, polycarboxylates, for example polyacrylic acid or a partial sodium salt thereof or a copolymer of acrylic acid, for example a copolymer with maleic anhydride, cellulose ethers, particularly water-soluble or water-swellable cellulose ethers such as sodium carboxymethylcellulose, gelatin, agar, microcrystalline waxes, fatty acids or fatty alcohols having 12 to 20 carbon atoms and a melting point in the range 45 to 80°C, a monoester of glycerol and such a fatty acid, a mixture of a water insoluble wax having a melting point in the range from above 55°C to below 100°C and a water-insoluble emulsifying agent, glucose or hydrogenated glucose. A binder which is an organic compound having a melting point of from about 40 to 80°C and which in its liquid form is miscible with the polysiloxane containing polymer so as to form a homogeneous liquid which upon cooling forms a monophasic wax-like substance (that is a material which is homogeneous and shows no phase separation during the process or on storage of the granules) has the advantage of producing encapsulated antifoam granules of improved storage stability.

[0124] The surfactant used to disperse the silicone in the binder or encapsulant can be selected from the surfactants described above in connection with foam control emulsions. Silicone glycols are preferred for many binders, or fatty alcohol ether sulphate or linear alkylbenzene sulphonate may be preferred with a polyacrylic acid binder. The surfactant can be added to the silicone undiluted or in emulsion before the silicone is mixed with the binder, or the surfactant and silicone can successively be added to the binder.

[0125] Examples of carriers and/or supports are zeolites, for example Zeolite A or Zeolite X, other aluminosilicates or silicates, for example magnesium silicate, phosphates, for example powdered or granular sodium tripolyphosphate, sodium sulphate, sodium carbonate, sodium perborate, a cellulose derivative such as sodium carboxymethylcellulose, granulated starch, clay, sodium citrate, sodium acetate, sodium bicarbonate and native starch.

[0126] The foam control agents prepared in accordance to the method of the invention are useful for reducing or preventing foam formation in aqueous systems, particularly foam generated by detergent compositions during laundering, and are particularly useful in detergent compositions which have a high foaming characteristic, for example those based on high levels of anionic surfactants, e.g. sodium dodecyl benzene sulphonate to ensure effectiveness of detergent composition at lower washing temperatures, e.g. 40°C.

[0127] According to another aspect of the invention a detergent composition comprises (1) 100 parts by weight of a detergent component and (2) from 0.02 to 5 parts by weight of a foam control agent according to the first aspect of the invention.

[0128] Suitable detergent components comprise an active detergent, organic and inorganic builder salts and other additives and diluents. The active detergent may comprise organic detergent surfactants of the anionic, cationic, non-ionic or amphoteric type, or mixtures thereof. Suitable anionic organic detergent surfactants are alkali metal soaps of higher fatty acids, alkyl aryl sulphonates, for example sodium dodecyl benzene sulphonate, long chain (fatty) alcohol sulphates, olefine sulphates and sulphonates, sulphated monoglycerides, sulphated esters, sulphonated or sulphated ethoxylated alcohols, sulphosuccinates, alkane sulphonates, phosphate esters, alkyl isethionates, alkyl taurates and alkyl sarcosinates. Suitable cationic organic detergent surfactants are alkylamine salts, quaternary ammonium salts, sulphonium salts and phosphonium salts. Suitable non-ionic organic surfactants are condensates of ethylene oxide with a long chain (fatty) alcohol or fatty acid, for example C_{14-15} alcohol, condensed with 7 moles of ethylene oxide (Dobanol® 45-7), condensates of ethylene oxide with an amine or an amide, condensation products of ethylene and propylene oxides, sucrose esters, fluorosurfactants, fatty acid alkylol amides and fatty amine oxides. Suitable amphoteric organic detergent surfactants are imidazoline compounds, alkylaminoacid salts and betaines. Examples of inorganic components are phosphates and polyphosphates, silicates, such as sodium silicates, carbonates, sulphates, oxygen releasing compounds, such as sodium perborate and other bleaching agents and zeolites. Examples of organic components are anti-redeposition agents such as carboxymethylcellulose (CMC), brighteners, chelating agents, such as ethylene diamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA), enzymes and bacteriostats. Liquid detergent compositions may contain solvents, alkanolamines, pH adjusting agents, opacifiers, perfumes, dyes, colour stabilisers, bactericides, brighteners, soil release agents and/or softening agents.

[0129] The foam control agents are particularly useful in detergent compositions, for e.g. domestic laundering, dishwashing applications but may also be employed in personal care type applications such as hand wash applications and no rinse softeners such processes as paper making and pulping processes, textile dyeing processes, sewage treatment applications, cutting oil, coatings and other aqueous systems where surfactants may produce foam.

[0130] The emulsions and/or dispersions of the present invention can generally have a silicone loading in the range of about 1 to about 94 wt. %.

EXAMPLES

[0131] The following Examples are provided so that one skilled in the art will more readily understand the invention. Viscosity measurements of the polymer products were carried out using a Brookfield Viscometer, spindle 6, at 10rpm. Unless otherwise indicated, all parts and percents are by weight and all viscosities are at 25°C.

EXAMPLE 1

[0132] A silicone-based foam control agent was prepared by polymerizing 50 parts by weight of dimethyl hydroxyl terminated polydimethylsiloxane having a viscosity of 72 mPa.s in 50 parts by weight of Hydroseal$^{(R)}$ G 250H (sold by Total Belgium of Brussels Belgium) using 2.4 parts by weight of DBSA. The polymerization was stopped once a viscosity of 52000 mPa.s was reached by the addition of 1.54 parts of triethanolamine (TEA).

[0133] Subsequent to completion of the reaction components silica (b) and, if required, resin (c) where introduced into the resulting product

b) 4% by weight of Sipernat® D10 (sold by Degussa GmbH); a commercially available precipitated silica with a surface area of 200g/m^2 which has been hydrophobically treated;

c) 3% by weight of an organosilicon resin having an M:Q ratio of 0.65:1. The organosilicon resin was introduced into the composition , in a trimethylsilyl terminated polydimethylsiloxane having a viscosity of 1000 mPa.s at 25°C in a resin: siloxane ratio of 25:75.

[0134] Emulsified foam control compositions containing (b) alone or alternatively (b) in combination with (c) above were prepared using the following process:

[0135] 105 parts of the appropriate foam control composition were placed in suitable receptacle and heated to 60°C. A mixture of 9.3 parts of Volpo® S2 and 9.3 parts of Volpo® S20 (sold by Croda NV) surfactants was preheated to 60°C and mixed in with the foam control composition.

[0136] A mixture [M] consisting of
0.76 parts of xanthan gum (used as a thickener),
2.32 parts of Natrosol® 250LR, (a hydroxyethylcellulose sold by the Aqualon Division of Hercules Inc of USA)
0.16 parts of sorbic acid,
0.32 parts of benzoic acid,
0.77 parts of a 10% solution of sulfuric acid and
95.66 parts of water was prepared.

[0137] The organic acids in the composition function as preservatives and sulphuric acid is used as a preservative and as a pH controlling agent.

[0138] 45 parts of mixture [M] was added to the receptacle and after thorough mixing, another 112 parts of mixture [M] were added and mixed in. Finally 219.5 parts of water were added resulting in a suitable emulsion of the foam control composition.

SHAKING TEST – SAMPLE PREPARATION

[0139] As a test of the capability of the resulting emulsions samples were tested with a simple shaking test. A 1% by weight solution of surfactant (as indicated below) in water was prepared and 100ml of the solution was placed in a 250ml closed bottle. 10µl of the prepared antifoam composition emulsion was introduced into the closed bottle to produce the sample to be tested. In Table 1 below the surfactants used were DBSA in samples 1A and 1B and Triton® X-100 in Samples 1Cand 1D. Emulsions 1A and 1C contained silica but no resin. Emulsions 1B and 1D contained both silica and resin.

SHAKING TEST – TEST PROCEDURE

[0140] The bottle containing a sample prepared as described above was shaken using a commercial shaker for periods of 8, 32, 48 and 96 seconds at 400 strokes per minute. After shaking the following were observed:-

- foam level (0 - 100%). This is the percentage of the original free space in the container filled with foam after shaking for the period indicated in Table 1a.

- collapse time to 10% - this is the time taken for the foam to collapse back to10 % of the volume of free space in the container before shaking commences for the period indicated in the Table.1a

Table 1 a

Sample					
1A	Shaking	8s	32s	48s	96s
	Foam Height (%)	50	75	100	100
	Collapse 10% (s)	6	10	19	78
1B	Shaking	8s	32s	48s	96s
	Foam Height (%)	75	100	100	100
	Collapse 10% (s)	80	97	90	80
1C	Shaking	8s	32s	48s	96s
	Foam Height (%)	25	50	50	75
	Collapse 10% (s)	22	41	50	41
1D	Shaking	8s	32s	48s	96s
	Foam Height (%)	25	50	50	75
	Collapse 10% (s)	27	20	21	26

GRANULATION

[0141] A granulated foam control agent was prepared using a foam control agent prepared in accordance to the method of the present invention in Example 1 which incorporated both (b) Sipernat® D10 and (c) the organosilicon resin. using the following process: 63g of an acrylic/maleic copolymer sold as Sokalan® CP5 from BASF was initially added to 42 g of water whilst mixing. Once the resulting mixture was homogeneous 12g of DBSA and 37g of the foam control agent prepared above was added whilst mixing continued. The resulting mixture was then added to zeolite powder in an agglomeration mixer until a desired average granule particle size was achieved (typically 55g of liquid on 100g of powder). The resulting granular products were dried in a fluid bed to remove the excess water and classified to remove any undesirable fines or oversized granules.

[0142] The resulting granulated product was tested in a standard European style front loading washing machine (Miele®) which was loaded with 2.5kg of clean cotton fabric. The wash tests were carried out at 40°C using 14 liters of water (hardness of 19°F) per wash.

[0143] The detergent composition used comprised:
6.9 parts by weight of sodium dodecylbenzenesulfonate anionic surfactant (Maranil paste A sold by Cognis)
5.1 parts by weight of nonionic surfactants (dehydol LT7 sold by Cognis)
42.9 parts by weight of zeolite 4A
5.1 parts by weight of sodium sulphate
15 parts by weight of sodium carbonate
15 parts of by weight of sodium perborate tetrahydrate

[0144] The granulated antifoam was added in an amount of 0.4% by weight of the detergent composition, to 90g of the detergent powder. The foam height of foam was observed every 5 minutes throughout each wash test (0 = no foam, 50 = half window of foam, 100 = full window of foam). The results are shown in Table 1b below:

Table 1b

Time (min.)	0	5	10	15	20	25	30	35	40	45	50	55	60
Foam Height %	0	0	0	0	0	0	15	40	60	75	85	95	100

EXAMPLE 2

[0145] A silicone-based foam control agent was prepared by polymerizing 50 parts by weight of dimethyl hydroxyl terminated polydimethylsiloxane having a viscosity of 72mPa.s in 50 parts by weight of trimethylsilyl terminated polydimethylsiloxane (100mPa.s) using 2.4 parts by weight of DBSA in the presence of 3 parts by weight of Sipernat® D10. The polymerization was stopped once a viscosity of 38000 mPa.s was reached by the addition of 1.5g of TEA.

[0146] Subsequent to completion of the reaction component samples of the resulting product were tested using the shaking method described in Example 1.

[0147] In Table 2 below the surfactant used was DBSA in Samples 2A and Triton® X-100 in Sample 2B.

TABLE 2

Sample					
2A	Shaking	8 s	32 s	48 s	96 s
	Foam height (%)	100	75	100	100
	Collapse 10% (s)	10	7	9	15
2B	Shaking	8 s	32 s	48 s	96 s
	Foam height (%)	50	50	50	75
	Collapse 10% (s)	6	6	9	30

A granular form of the foam control agent produced in accordance with the present invention was prepared by the method described in Example 1.

EXAMPLE 3 :

[0148] A silicone-based foam control agent was prepared by polymerizing 48.5 parts by weight of dimethyl hydroxyl terminated polydimethylsiloxane having a viscosity of 72mPa.s in 48.5 parts by weight of an organic extender (Hydroseal G250H) using 2.4 parts by weight of DBSA in the presence of 3 parts by weight of Sipernat® D10. The polymerization was stopped once a viscosity of 68000 mPa.s was reached by the addition of 1.5 parts by weight of TEA.

[0149] Subsequent to completion of the reaction component samples of the resulting product were tested using the shaking method described in Example 1.

[0150] In Table 3 below DBSA was the surfactant used in Sample 3A and the surfactant used in Sample 3B was Triton® X-100.

TABLE 3

Sample					
3A	Shaking	8 s	32 s	48 s	96 s
	Foam height (%)	100	100	100	100
	Collapse 10% (s)	90	10	14	54
3B	Shaking	8 s	32 s	48 s	96 s
	Foam height (%)	25	25	50	75
	Collapse 10% (s)	5	7	7	18

[0151] A granular form of the foam control agent produced in accordance with the present invention was prepared by the method described in Example 1.

COMPARATIVE EXAMPLE 1

[0152] In order to assess the foam control of products prepared in accordance with the process of the present invention, emulsions of two commercial antifoams, Dow Corning® DB 100 and Dow Corning® 3990 (sold by Dow Corning Corporation of Michigan, USA) were prepared using the method described in example 1 above. The samples prepared were analysed using the shake test described in example 1 above and the results are provided below in Table CE1.

TABLE CE1

Antifoam	Surfactant					
DB-100	DBSA	Shaking	8 s	32 s	48 s	96 s
		Foam height (%)	60	100	100	100
		Collapse 10% (s)	>120	>120	>120	>120
3990	DBSA	Shaking	8 s	32 s	48 s	96 s
		Foam height (%)	50	75	75	100
		Collapse 10% (s)	>120	13	29	60
DB-100	Triton® X-100	Shaking	8 s	32 s	48 s	96 s
		Foam height (%)	50	50	60	75
		Collapse 10% (s)	>120	30	29	31
3990	Triton® X-100	Shaking	8 s	32 s	48 s	96 s
		Foam height (%)	50	50	50	60
		Collapse 10% (s)	>120	17	19	27

[0153] Whilst production costs of materials prepared in accordance with the present invention are significantly lower than for the commercial products tested, it was found that the foam control provided by the compositions prepared in accordance with the present invention was comparable and in some instances better than the foam control achieved when testing commercial products tested.

EXAMPLE 4 :

[0154] 5 different samples of foam control agents were prepared in accordance with the process of the present invention and these were subsequently compared with the performance of a commercial antifoam product Dow Corning$^{(R)}$ 3990

Step A

Mixtures of diluents in the following proportions were prepared for the respective samples 4a- 4c

a) 405.4 parts by weight of parts by weight of trimethylsilyl terminated polydimethylsiloxane (1000mPa.s) and 1125 parts by weight of Hydroseal® G250H;

b) 280.4 parts by weight of trimethylsilyl terminated polydimethylsiloxane (1000mPa.s) and 250 parts by weight of Hydroseal® G250H;

c) 155.4 parts by weight of trimethylsilyl terminated polydimethylsiloxane (1000mPa.s) and 375 parts by weight of Hydroseal® G250H; and

[0155] Step B Foam control compositions (Samples 4a – 4c) were prepared by mixing:

- 530.4 parts of the respective mixture prepared in Step A
- 32 parts of Sipernat D10
- 228.4 parts of a dimethylvinylsiloxane end-blocked polydimethyl siloxane having a viscosity of 9000 mPa.s,
- 2.0 parts of a trimethylsiloxane end-blocked copolymer of dimethylsiloxane units and methylhydrogensiloxane units, having a viscosity of about 7 mPa.s and 0.3% by weight of Si-H groups
- 6.4 parts of a 24% mixture of resinous polyorganosiloxane having a molecular weight of about 13,000 and trimethyl siloxy end-groups and 69% of a trimethyl end-blocked polydimethyl siloxane having a viscosity of 1000 mPa.s,
- 0.8 parts of a catalyst which was a chloroplatinic acid complex of divinyltetramethyldisiloxane diluted in 70% by weight of dimethylvinylsiloxy endblocked polydimethylsiloxane.

[0156] In step B the ingredients were mixed (Hauschild Speedmixer) and left to react at a temperature of 60°C for 1 hour. The resulting mixture was homogenised before 200 parts of trimethyl siloxane end-blocked polydimethyl siloxane having a viscosity of 1000 mPa.s and containing 0.45% by weight of 1-ethynylcyclohexanol were added into the compound.

FOAM CELL TESTS

[0157] The resulting products and the comparative were emulsified as described in Example 1 and their respective performance was analysed by means of a so-called "foam cell test";

TEST CONDITIONS

[0158] The emulsified foam control compositions were tested in a foam cell using a softwood liquor. To this effect 600 ml of softwood liquor is preheated at 90°C and introduced in a graduated and thermostatically controlled glass cylinder having an inner diameter of 5 cm. This foamable liquid was circulated through a circulation pipe at a temperature adjusted to 89°C. The circulation flow rate is controlled using a MDR Johnson pump set up at a frequency of 50 Hz. When the foam height of 30 cm is reached, 150 µl of emulsion of the tested foam control composition is injected in the liquid jet. The evolution of the foam height was monitored and recorded. The foam height was measured in cm over a sufficient period to allow the foam control composition to have exhausted its capacity, which is when the foam height of 29cm has been reached again in the foam cell, and the time at which this occurred was measured as it indicates the longevity of the foam control composition.

RESULTS

TABLE 4 IS A MEASURE OF FOAM HEIGHT (FH) IN CM AGAINST TIME FOR A (COMPARATIVE) COMMERCIAL PRODUCT AND EXAMPLES 4A TO 4C AS DESCRIBED ABOVE.

TABLE 4

Time (sec)	FH (cm) CP	FH (cm) 4a	FH (cm) 4b	FH (cm) 4c
0	30	30	30	30
10	15.5	25	26	28
20	14.5	21	19	25
30	22.5	19.5	18.5	21.5
40	19	21	18	20
50	18.5	20.5	19	20.5
60	20	22.5	19.5	20.5
70	20.5	23.5	22.5	21.5
80	20.5	24.5	24.5	24
90	22	24	25.5	25.5
100	22.5	25	25	25.5
110	24.5	25.5	25.5	26
120	25.5	26	26	26
130	24.5	25.5	25.5	26.5
140	25	25.5	24.5	26
150	26.5	26	26.5	27.5
160	25.5	26.5	25	25.5
170	26.5	26.5	25.5	24.5
180	27	27	26.5	25
190	27.5	27.5	26.5	25.5
200	28.5	27.5	27.5	26
210	28.5	28	27.5	26.5
220		28.5	28	26.5
230		28.5	28.5	27
240		28.5	28.5	27.5
250		29	28.5	28.5
260			28.5	28.5
270			29	28.5
280				28.5
290				28.5
P300				29

It was identified that the maintenance of foam control was comparable and in some instances even better than the comparative commercial material tested.

CLAIMS

1. A method of making silicone-based foam control agents comprising
   (i) preparing a polysiloxane containing polymer by the polymerisation of siloxane containing monomers and/or oligomers in the presence of an inert organopolysiloxane and/or an organic fluid, a suitable catalyst and optionally an end-blocking agent;
   (ii) where required quenching the polymerisation process; wherein the inert organopolysiloxane and/or an organic fluid,is substantially retained within the resulting diluted polysiloxane containing polymer;
   (iii) introducing from 0.1 to 10 % by weight of a suitable filler prior to during or subsequent to step (i);
   (iv) optionally introducing up to 5% by weight of a suitable silicone resin during or subsequent to step (i) and
   (v) where required, adapting the foam control agent produced in steps (i) to (iv) into a suitable form of delivery therefor.

2. A method in accordance with claim 1 characterised in that the inert fluid is an organic extender and/or plasticiser

3. A method according to claim 1 characterised in that the inert fluid is an organopolysiloxane which does not react with cyclic siloxane having from 2 to 20 silicon atoms.

4. A method according to claim one characterised in that the inert fluid is a trialkylsilyl terminated polydialkylsiloxane having a viscosity of from 0,65 to 10000mPa.s at 25°C.

5. A method in accordance with any preceding claim characterised in that the siloxane containing polymer is prepared via a polymerisation process selected from the group of polycondensation, chain extension, polyaddition, and ring opening

6. A method according to claim 5 characterised in that the polymer is prepared via a polycondensation reaction with dodecylbenzenesulphonic acid as catalyst.

7. A method in accordance with any preceding claim characterised in that the polymer is of the following general formula

$$R_{(3-a)}R^1_aSiO[(R_2SiO)_b(RR^1SiO)_c]SiR_{(3-a)}R^1_a \qquad (1)$$

wherein each R is the same or different and is an alkyl group containing 1-8 carbon atoms, a substituted alkyl group containing 1 to 6 carbon atoms or a phenyl group; R^1 is a hydroxy group, a hydrolysable group, an unsaturated organic group; a is zero or 1, b is an integer and c is zero or an integer and the sum of b + c is equal to a value of at least 200.

8. A method in accordance with claim 10 characterised in that the sum of b + c is equal to a value of at least 1500.

9. A method according to any of Claims 1 to 8 characterised in that the organosilicon resin is a non-linear silicone consisting of siloxane units of the formula $R'_aSiO_{4-a/2}$ wherein R' denotes a hydroxyl, hydrocarbon or hydrocarbonoxy group, and wherein *a* has an average value of from 0.5 to 2.4.

10. A method according to Claim 9, characterised in that organosilicon resin is a siloxane resin consisting of monovalent trihydrocarbonsiloxy (M) groups of the formula $R''_3SiO_{1/2}$ and tetrafunctional (Q) groups $SiO_{4/2}$ wherein R" denotes a monovalent alkyl group and the number ratio of M groups to Q groups is in the range 0.4:1 to 1.1:1.

11. A method in accordance with any preceding claim wherein the foam control agent is prepared in the form of an oil-in-water emulsion utilising the additional steps:-

(V) if required, introducing one or more surfactants into the polysiloxane containing polymer to form a homogenous oil phase;
(VI) adding water to the homogenous oil phase to form a water-in-oil emulsion, the water being added in an amount of 0.1 -10 percent by weight based on total oil phase weight;

(VII) applying shear to the water-in-oil emulsion to cause inversion of the water-in-oil emulsion to an oil-in-water emulsion; and optionally

(VIII) diluting the oil-in-water emulsion by adding more water.

12. A method in accordance with any one of claims 1 to 10 wherein the foam control agent is prepared in the form of an water-dispersible foam control composition by dispersing the product resulting from the process in any of claims 1 to 8 in a in a water-dispersible carrier.

13. A method in accordance with any one of claims 1 to 10 wherein the foam control agent is prepared in the form of a granulated foam control agent by involving the product of the process in any one of claims 1 to 10 in one or more of the following methods granulation, spray drying, emulsification followed by drying, spray mixing, spray chilling, compacting, extrusion, high shear mixing and/or low shear mixing and flaking.

14. A method in accordance with claim 13 characterised in that the granulated foam control agent prepared is supported on a particulate carrier.

15. A method according to Claim 14, characterized in that a water-soluble or water-dispersible binder is deposited on the particulate carrier.

16. A method according to any preceding Claim, characterised in that hydrophobic filler is selected from the group consisting of silica, titania, ground quartz, alumina, aluminosilicates, polyethylene waxes, microcrystalline waxes, zinc oxide, magnesium oxide, salts of aliphatic carboxylic acids, cyclohexylamine, alkyl amides and SiO_2.

17. A method according to Claim 16, characterised in that filler is a silica filler with an average particle size of from 0.5 to 30μm.

18. A method according to any of Claims 1 to 17, characterised in that organosilicon resin is present at 2 to 30% by weight based on polysiloxane containing polymer.

18. A foam control agent according to any of Claims 1 to 17, which is provided in the form of an oil-in-water emulsion.

19. A water-dispersible foam control composition comprising a foam control agent according to any of Claims 1 to 17 dispersed in a water-dispersible carrier.

20. A foam control agent in particulate form in accordance with Claim 13.

21. A foam control agent according to Claim 20, characterised in that the particulate foam control agent additionally comprises a binder or encapsulant and a carrier or support.

22. A foam control agent according to Claim 21, characterised in that the binder is a polyoxyalkylene polymer, a polycarboxylate polymer or a cellulose ether.

23. A foam control agent according to Claim 21, characterised in that the binder is an organic compound having a melting point of from about 40 to 80°C and which in its liquid form is miscible with the polysiloxane containing polymer so as to form a homogeneous liquid which upon cooling forms a monophasic wax-like substance.

24. A foam control agent according to any of Claims 21` to 23 characterised in that the carrier is a zeolite, sodium tripolyphosphate, sodium sulphate, sodium perborate, or sodium carbonate.

25. A foam control agent in the form of an water-dispersible foam control composition in accordance with claim 12.

26. A foam control agent in the form of a an oil-in-water emulsion method in accordance with claim11.

27. A detergent composition characterised in that it comprises 0.01 to 5% by weight of a foam control agent according to any one of the preceding claims based on the detergent component.