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(54) **Title:** COMPOSITION OF FLUORINATED SILICONES, PARTICULARLY BUT NOT EXCLUSIVELY FOR ADHESIVE-RELEASING COATINGS, AND PREPARATION THEREOF

(57) **Abstract:** A composition comprising two classes of fluorinated silicones, termed respectively POS1. and POS2, and a hydrosilylation catalyst. The two fluorinated silicones are characterized by an orderly and repeated arrangement of the individual monomers and by the presence of different reactive groups, which can react with each other at mixing time, producing the crosslinking of the mass. The composition is particularly suitable for the preparation of supports for temporary adhesion of adhesive articles. The two classes of fluorinated silicones and methods for their preparation are also described.

COMPOSITION OF FLUORINATED SILICONES, PARTICULARLY BUT NOT EXCLUSIVELY FOR ADHESIVE-RELEASING COATINGS, AND PREPARATION THEREOF

Technical field

The present invention relates to a new composition of fluorinated silicones, particularly for the preparation of substrates for temporary adhesion of adhesive articles, and to the preparation of the individual fluorinated silicones comprised in the composition.

Background art

In industrial practice it can be necessary to render non-adhesive the surface of certain materials, for example when the materials are to be used as temporary supports for adhesive articles. In the continuation of this text, the expression "temporary support" will be used as a synonym of "temporary adhesion support".

The treatment of the surfaces that act as support must make them adapted to firmly but temporarily fix the adhesive articles applied thereto but also to release them during use with the least possible effort and without reducing their adhesiveness characteristics.

Patents EP 850999, US 4,736,048, US 4,889,753 have achieved the per se opposite effects of fixing and prompt release of the adhesive articles by applying to the supporting surface a mixture of fluorinated silicon polymers. In these patents, and particularly in US 4,889,753, the applied mixture comprises two polymers, only one of which is fluorinated; said polymers are made to react, providing a more complex polymer. The reaction is based on the addition (hydrosilylation reaction) of the Si-H groups of one of the two polymers to double bonds that are instead provided on the second polymer. This reaction is discussed for other purposes also in US 2,637,738, US 4,591,622, US 6,403,105 and US 6,265,515.

The various silicone polymers involved in the reaction are obtained by random polymerization of a mixture of monomers, in which the various

alkenyl, alkyl and perfluoroalkyl functional groups assume a disorderly arrangement along the molecule.

Known fluorinated silicone compositions suffer several up to now acknowledged drawbacks, which can be ascribed for example to a partial mutual incompatibility of the individual polymers that constitute them, which causes a partial transfer (migration) of the silicone layer to the adhesive article once it is removed, to an irregular structure of the silicone polymer, which leads to a performance that is not always adequate, to the lack of reproducibility and repeatability of the results in terms of effort to remove the applied adhesive articles.

Disclosure of the Invention

Therefore, the aim of the invention is to provide a composition comprising fluorinated silicone polymers that overcomes the drawbacks of the background art.

Within this aim, an object of the present invention is to provide a composition of fluorinated silicones that is particularly adapted to obtain temporary supports for adhesive articles and that in particular allows a firm anchoring of the adhesive articles on any polymeric film and at the same time allows their easy separation with minimal effort.

Another object is to provide a composition comprising fluorinated silicones in which the mutual compatibility and the performance of the individual components of the composition are improved.

An object of the invention is also to provide fluorinated silicone polymers that have a highly defined structure and whose combination is particularly suitable for the preparation of a composition as defined above.

Another object is to provide a temporary support for adhesive articles that overcomes the drawbacks of the background art.

Another object is to provide a method for producing said fluorinated polymers that allows in particular to achieve fine control of their structure, allowing to modify at will their chemical and physical properties and most of

all their surface tension.

Another object of the invention is to provide a method for preparing said fluorinated silicone composition.

This aim and these and other objects are achieved by a compound as defined in claim 1.

The aim and objects of the invention are further achieved by a composition as defined in claim 8.

The aim and objects of the invention are further achieved by a crosslinked composition as defined in claim 17.

The aim and objects of the invention are further achieved by a laminated element as defined in claim 18.

The aim and objects of the invention are further achieved by a method as defined in any one of claims 20, 29, 36, 41 and 52.

Ways of carrying out the Invention

In a first aspect, the present invention relates to a composition comprising:

a) at least one fluorinated silicone (polyorganosiloxane), designated here by the acronym POS1, which has, along the silicone chain, at least two –Si–H reactive groups;

b) at least one fluorinated silicone (polyorganosiloxane), designated here by the acronym POS2, which has, along the silicone chain, at least two $-CH=CH_2$ reactive groups;

c) at least one catalyst of the hydrosilylation reaction.

Optionally, the POS have, along the chain, other chemical groups adapted to modify their chemical and physical properties, such as for example epoxy groups.

The presence of other additives, such as surfactants and stabilizers (also known as inhibitors) is preferred but optional.

In a second aspect, the present invention describes subclasses of POS1

and POS2 and advantageous methods for synthesizing them. The methods according to the invention allow to create block polymers (both POS1 and POS2) in which the fluorinated units are distributed in an orderly manner along the silicone chain so that the structure of the polymers is highly repeatable, this being an aspect that clearly distinguishes the present invention from known methods, which are instead unable to lead to repeatable sequences of monomers. Moreover, by being able to control finely the quantity and position of the fluorine atoms within the polymer, it is also possible to modify at will the chemical and physical properties (and in particular the surface tension) of the final fluorinated composition in which the two polymers will be introduced. The viscosity of the polymers POS1 and POS2 is a very important aspect for obtaining a final composition that has a particularly high performance.

In a third aspect, the present invention describes a new fluorinated silicone polymer provided starting from the composition comprising the POS1 and POS2 and the method for its preparation. In particular, the polymer according to the invention is obtained by crosslinking the two separate silicone polymers (basic components), in which the first one, POS2, is characterized by the presence, in the chain, of alkenyl groups (of any type, preferably vinyl and allyl), and the other one, POS1, is characterized by the presence of Si–H groups and acts as a crosslinking agent with respect to the POS2. In the presence of one or more appropriate hydrosilylation catalysts and advantageously also of heat, the Si–H groups react with the $-CH=CH_2$ groups, producing the crosslinking.

In a fourth aspect, the present invention relates to a support particularly for the temporary application of adhesive articles, comprising one or more layers of a fluorinated silicone composition obtained by crosslinking a composition as defined above, applied to a foundation having a polymeric matrix such as for example polyethylene terephthalate, polytetramethylene terephthalate, polyethylene 2,6–naphthalate,

polyethylene–1,4–cyclohexylene, dimethylene terephthalate, polyethylene terephthalate/adipate, polyethylene terephthalate/sebacate, polypropylene, PVC, polypropylene, and mixtures thereof.

In a further aspect, the present invention relates to the products obtainable by the synthetic methods that will be disclosed below.

A first ingredient of the composition according to the invention is constituted by the POS1 compounds. POS1 is used to designate a polyalkyl hydrosiloxane compound in which some hydrogens are substituted by a functionality provided with a semi- or perfluorinated alkyl group. The present invention describes three different types of POS1 compounds, termed respectively POS1A, POS1B and POS1C, and synthesis thereof.

A first class of POS1 compounds useful in the provision of the invention is constituted by the ones designated here as POS1A. These compounds have the general formula (1A):

$$(R')(R)_2Si–O–[(H)_{1-k}(Z_1)_kSi(R)O–]_{f1}–[(H)_{1-y}(Z_2)_ySi(R)O–]_{f2}–Si(R)_2(R')$$

where:

R is C1–C10 alkyl, preferably C1–C3 alkyl, more preferably methyl or ethyl;

R' is R or hydrogen,

f_1 is a whole number comprised between 1 and 200;

f_2 is a whole number comprised between 0 and 100;

k is 0 or 1 where if f_1 is 1, k is 1

if f_1 is 2, k is 1 in at least one repetition of the monomer f_1,

if f_1 is comprised between 3 and 200, in each repetition of the monomer f_1, k is independently 0 or 1, assuming that k is 1 in at least one monomer f_1,

y is 0 or 1,

A is selected from the group consisting of:

i) –CH=CH–,

ii) $-C_2H_4-$,

iii) $-C_3H_6-$,

iv) $-(CH_2)_q-$, where q is a whole number comprised between 1 and 9;

v) $-CH(CH_3)CH_2-$ bound to the silicon by means of the right end, and

vi) $-CH(CH_2CH_3)CH_2-$ bound to the silicon by means of the right end;

B is absent or selected from the group consisting of –O–, –S–, and –NH–;

E is absent or is selected from the group consisting of

i) $-CH_2CH_2-$,

ii) –CH=CH–,

iii) $-CH=CH-CH_2-$,

iv) $-CH_2CH_2CH_2-$,

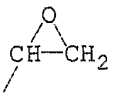
v) $-CH_2CH(OCH_3)CH_2-$,

vi) $-(CH_2)_m$ C(O)–, bound to B by means of the right end, and m is a whole number comprised between 0 and 10;

vii) $-(CH_2)_v-O-C(O)-$, v is a whole number comprised between 2 and 18;

Z_1 is a –A–B–E–RF group, where RF is a $C_nF_{2n+1}-$ group in which n is a whole number comprised between 2 and 20, preferably between 6 and 16, and more preferably RF is a C4–C18 perfluoroalkyl group;

Z_2 is a –A–B–D group, where D is an epoxy group selected between:

ethylene oxide, 

and

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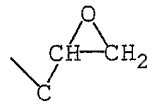


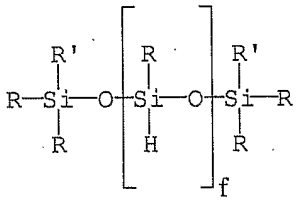
propylene oxide

assuming that y, k and R' are such that there are at least two Si-H groups for each POS1A molecule.

A preferred POS1A polymer has a viscosity comprised between 100 and 300 cP, preferably comprised between 150 and 250 cP.

The term "monomer f1" is used to designate the portion of the POS1A molecule enclosed within the brackets with the subscript f1.

In a further aspect, the invention relates to the synthesis of the POS1A compounds. The method of synthesis comprises the step of reacting a compound having the general formula (I-1A):



where f is (f_1+f_2) and preferably is a whole number comprised between 3 and 200, more preferably comprised between 30 and 40; R and R' are defined as above;

with at least one fluorinated compound selected from the group consisting of:

1) fluorinated terminal olefins, optionally comprising, within the chain, a heteroatom selected among oxygen, nitrogen or sulfur, preferably olefins selected from the group consisting of:

i) $C_nF_{2n+1}CH=CH_2$,

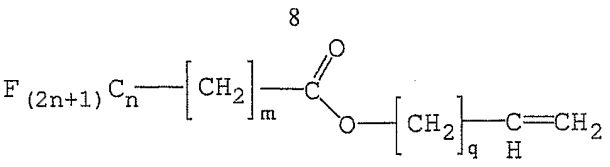
ii) $C_nF_{2n+1}CH_2CH=CH_2$,

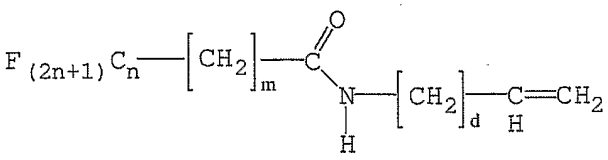
iii) $C_nF_{2n+1}(CH_2)_2O(CH_2)_q$ $CH=CH_2$,

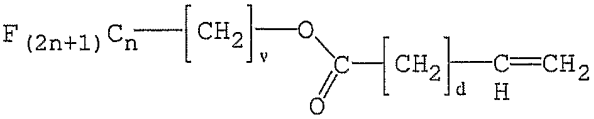
iv) $C_nF_{2n+1}(CH_2)_2OCH_2C_6H_4$ $CH=CH_2$,

v) $C_nF_{2n+1}(CH_2)_2S(CH_2)_q$ $CH=CH_2$,

vi) $C_nF_{2n+1}CH_2$ $CH(OCH_3)CH_2O(CH_2)_q$ $CH=CH_2$,

vii) 

viii) 

ix) 

where n, m, v and q are defined as above and d is either any integer comprised between 0 and 3, or a specific integer comprised between 0 and 3 as it will be indicated in each occasion;

2) fluorinated primary alcohols, optionally comprising within the chain a heteroatom selected among oxygen, nitrogen or sulfur, preferably alcohols having the formula $C_nF_{2n+1}(CH_2)_l$–OH, where n is defined as above and l is an integer comprised between 2 and 10.

Optionally, the compound (I–1A) is reacted not only with the fluorinated derivative but also with one or more epoxy derivatives, preferably epoxidized terminal olefins, more preferably at least one of the olefins selected among:

i) D–$(CH_2)_g$–CH=CH_2,

ii) D–$(CH_2)_d$ –O–$(CH_2)_g$–CH=CH_2,

iii) D–$(CH_2)_d$ –S–$(CH_2)_g$–CH=CH_2,

where g is a whole number comprised between 1 and 20 and d is defined as above. The terminal epoxy group is designated by the letter D in the formulas given here. If the olefin comprises a free terminal epoxy group (D), after the reaction with the Si–H group of the compound (I–1A) it will form the ≡S_i–Z_2 radical described earlier.

The molar ratio between the fluorinated compound and the compound

having the formula (I–1A) is comprised between 1 and 100, preferably between 5 and 20, while for 1 mole of fluorinated compound it is possible to add 0 to 0.5 moles of epoxy derivative.

The polyalkyl hydrosiloxane having the formula (I–1A) is preferably selected among:

i) polymethyl hydrosiloxanes,

ii) polyethyl hydrosiloxanes,

iii) copolymers of (methyl–hydro)–(dimethyl hydrosiloxanes), such as for example poly(dimethylsiloxane–co–methylhydrosiloxane), and

iv) mixtures thereof.

If fluorinated olefins are used, the reaction is preferably performed in a nitrogen atmosphere and at a temperature comprised between 100°C and 150°C. Moreover, the reaction is performed advantageously in the presence of a catalyst, such as for example one or more organic peroxides, preferably t-butyl peroxide and benzoyl peroxide.

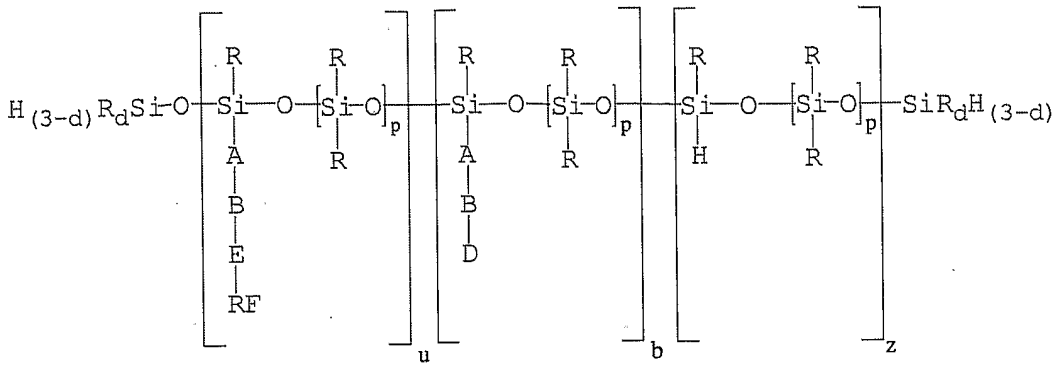
If the olefin has a boiling point that is lower than approximately 60°C, the catalyst is advantageously a platinum-based catalyst, such as chloroplatinic acid in solution in 2-propanol. In this case, the reaction occurs at the reflux temperature of the olefin and it is then necessary to filter the reaction crude after the olefin has disappeared, so as to remove the Pt° that has formed.

If instead fluorinated alcohols are used, the preferred catalysts are catalysts based on tin, cobalt, copper and zinc, such as for example stannous octoate, dibutyl tin dilaurate, zinc octoate or copper naphthenate. The reaction generates hydrogen and therefore is performed under a constant stream of nitrogen in order to dilute the hydrogen and remove it from the reaction environment.

The length of the chain of the olefins and of the fluorinated alcohols will influence the chemical and physical properties of the final composition, in that a higher number of fluorine atoms incorporated in the polymer is

matched by a greater reduction in the surface tension of the final composition.

A second class of POS1 compounds useful for providing the invention is constituted by the ones termed here POS1B. These compounds have the general formula (1B):



where:

u is a whole number comprised between 1 and 400, preferably comprised between 10 and 200;

b is a whole number comprised between 0 and 400;

z is a whole number comprised between 2 and 400, preferably comprised between 10 and 200;

p is a whole number and is comprised between 3 and 100, preferably comprised between 7 and 14, more preferably equal to 7;

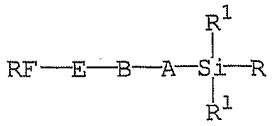
R, RF, A, B, E, D and d are defined as above.

A preferred POS1B polymer has a viscosity comprised between 80 and 180 cP.

In a further aspect, the invention relates to the synthesis of the compounds POS1B. The method comprises a first step of synthesis of the basic fluorinated monomer, a second step of polymerization of the monomers so as to form the silicon skeleton of the polymer, a third step of elongation of the chains and a fourth step for terminating polymerization, with blocking of the reactive groups.

The first step i) prepares a fluorinated monomer (a–1B) having the

general formula:



where A, B, E, R and RF are defined as above, and R^1 is selected between –Cl and –OR, where R is defined as above.

In a first embodiment, the heteroatom constituted by the radical B is oxygen or –NH–. In this embodiment a), the synthesis of (a–1B) occurs advantageously by placing in contact:

– at least one silicone unit having the general formula $H–SiR^1_{(3-d)}R_d$ where d is 1,

– with at least one compound selected between:

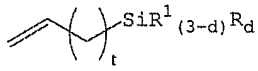
1) fluorinated terminal olefins, preferably one of the olefins indicated in relation to the POS1A compounds;

and, if R^1 is –OR, also

2) fluorinated primary alcohols, preferably one of the alcohols indicated in relation to the POS1A compounds.

In a different embodiment, the heteroatom constituted by the radical B is sulfur. In this embodiment b), the synthesis of (a–1B) occurs according to any of the two following methods:

b1) reacting:

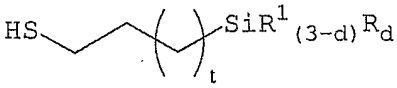
– a silicone unit having the general formula  where t is 0 or 1 and d is 1, R and R^1 are defined as above, with

– one or more primary fluorinated thiols, preferably thiols having the formula $C_nF_{2n+1}(CH_2)_l–SH$, where n and l are defined as above;

or

b2) reacting:

– at least one silicone unit having the formula

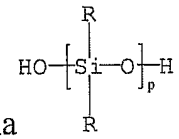


where d is 1, t, R and R_1 are defined as above, with

– at least one terminal fluorinated olefin, preferably one of the olefins i–ix) indicated in relation to the POS1A compounds.

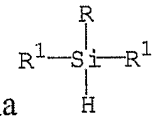
According to b1) and b2), the first step occurs advantageously in a solvent such as toluene, alkanes (for example hexane, heptane, octane, nonane), ethers (for example t-butyl methyl ether, diethyl ether, etc.) and mixtures thereof, in an atmosphere of nitrogen and in the presence of at least one catalyst preferably selected among organic peroxides and azonitrile compounds. The reaction is generally performed at between 60°C and 130°C, where the optimum temperatures are a function of the type of catalyst used.

The second step ii) comprises synthesizing the silicone skeleton of the POS1B polymer. For this purpose, the fluorinated monomer (a–1B) synthesized in the preceding step is mixed with:



– at least one silicone unit (b–1B) having the formula

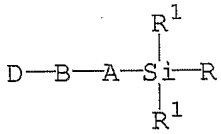
and



– at least one silicone unit (c–1B) having the formula

where p, R and R^1 are defined as above.

Optionally, but preferably, the mixture also receives the addition of a further monomer (d–1B) having the formula:



where the variables are defined as above.

For one mole of silicone unit (b–1B) it is possible to add 0.25 to 0.75 moles of fluorinated monomer (a–1B), 0.25 to 0.75 moles of silicone unit (c–1B) and 0 to 0.5 moles of silicone unit (d–1B).

When R^1 is chlorine, step ii) is advantageously performed under a

stream of nitrogen in order to remove the resulting hydrochloric acid and in a solvent preferably selected among toluene, hexane and heptane. The operating temperature is comprised between 30° and 80°C. The reaction time is comprised between 60 and 120 minutes.

If R^1 is alkoxy, step ii) is advantageously performed in a solvent preferably selected among toluene, hexane and heptane, at 60°-130°C, in a stream of nitrogen in order to remove the alcohol that has formed.

The third step iii) comprises forming the final chains and the fourth step iv) comprises ending the polymerization.

Step iii) substantially comprises bringing the reaction mixture of step ii) to a temperature comprised between 130°C and 150°C, at which the –OH or –OR groups condense together.

If R^1 is chlorine, however, it is necessary to precede step iii) with a preventive step of hydrolysis of the chlorines, so as to restore free –OH groups. This step can occur for example by washing the mixture obtained in the second step with water, subsequently removing the resulting HCl with further washes.

The step of actual condensation entails bringing the organic reaction mass to the temperature of 130°C-150°C in the presence of a strong acid, preferably trifluoroacetic acid, or of a base, such as strontium or barium hydroxide. This process can be performed in a stream of nitrogen in order to eliminate the water or R^1OH that forms in the reaction and is continued until the chosen degree of viscosity is reached.

Finally, the reaction is blocked (step iv) for example by adding a silicone unit (e–1B) having the formula:

$$R^1–SiR_dH_{(3-d)}$$

where d is an integer comprised between 0 and 3, R and R^1 are defined as above, preferably in a quantity comprised between 0.005 and 0.2 moles for 1 mole of silicone unit b–1B.

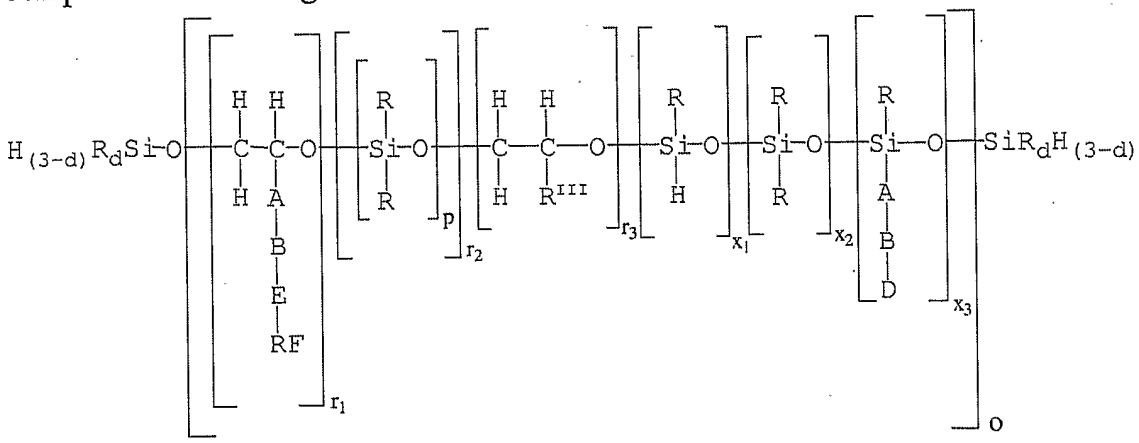
The unit (e–1B) reacts with the –OH or $–OR^1$ terminal groups that are

present, blocking their reaction capacity. The excess of the units (e–1B) is then easily removed for example by distillation.

In a different embodiment of the synthesis of POS1B, it is possible to add the unit (e–1B) already during step ii) (polymerization) in a quantity comprised between 0.002 and 0.1 moles per mole of silicone unit (b–1B). A shorter prepolymer is thus obtained.

The unit (b–1B) belongs to the class of hydroxy terminated polydimethylsiloxanes. There are various categories of silane unit (b–1B) characterized by different values of viscosity (i.e., characterized by different values of p). To provide the invention, it is possible to use units (b–1B) characterized by values of p comprised between 3 and 100, preferably comprised between 7 and 14, more preferably equal to 7. The choice of the monomer (b–1B) having the correct value of viscosity is a key aspect for obtaining the best performance of the product. If a unit with low viscosity is used, a larger quantity of hydroxyl groups available for condensation and a higher percentage of fluorine incorporated in the polymer are obtained.

A third class of POS1 compounds useful in the provision of the invention is constituted by the ones designated here as POS1C. These compounds have the general formula (1C):



where:

A, B, D, E, R, RF and d are defined as above,

R^{III} is hydrogen or a C_1–C_{20} alkyl group, preferably a C_1–C_4 alkyl group,

o is a whole number comprised between 10 and 600, preferably between 50 and 200, and

r_1, r_2, r_3, x_1, x_2, x_3, in each repetition of the oligomer o, are selected independently between 0 and 1, assuming that:

– r_1, r_2 and r_3 are not simultaneously 0,

– x_1, x_2, x_3 are not simultaneously 0,

– in at least two repetitions of the oligomer o, x_1 is 1, and

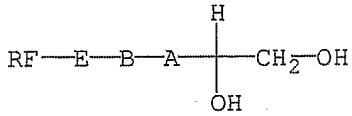
– in at least one repetition of the oligomer o, r_1 is 1.

A preferred POS1C polymer has a viscosity comprised between 10 and 40 cP.

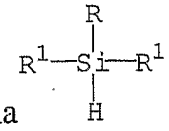
The term "oligomer o" is used to designate the portion of POS1C molecule enclosed between the brackets with the subscript o.

In a further aspect, the invention relates to the synthesis of the POS1C compounds. The method for producing them comprises a first step of polymerization of the basic monomers to form the skeleton of the polymer and a second step for ending the polymerization.

In a preferred embodiment, the first step (polymerization of the basic monomers) comprises reacting a fluorinated glycol (a–1C) having the general formula

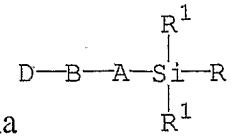


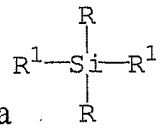
with at least one silicone unit (c–1C) having the formula



Optionally, but preferably, the mixture also receives the addition of at least one monomer selected between:

– monomer (d–1C) having the formula



– monomer (b–1C) having the formula 

In the POS1C, R^1 is chlorine while the other variables are defined as above. The fluorinated glycol (a–1C) can be used in any pure enantiomeric form or as a mixture of diastereoisomers.

In this first step it is possible to use the fluorinated glycol (a–1C), which can be used pure or in mixture with other non-fluorinated glycols such as propylene glycol, ethylene glycol, hexanediol and said silicone compound b–1B described above. Said non-fluorinated glycols are preferably present in a total quantity comprised between 0 and 0.5 moles for 1 mole of fluorinated glycol (a–1C).

For 1 mole of fluorinated glycol (a–1C) present, the silicone unit (b–1C) is advantageously present in a quantity comprised between 0 and 0.5 moles, the silicone unit (c–1C) is advantageously present in a quantity comprised between 0.25 and 1 moles, and the silicone unit (d–1C) is advantageously present in a quantity comprised between 0 and 0.5 moles.

This step is performed in a stream of nitrogen, at a temperature comprised between 30°C and 60°C, in a solvent selected among toluene, acetonitrile, t-butyl methyl ether and mixtures thereof. The reaction time varies between 60 and 180 minutes.

The second step is preceded by a preventive step of washing with water the reaction mass obtained in the first step, in order to convert the remaining Si–R^1 groups into Si–OH groups and remove the hydrochloric acid that has formed.

Then the Si–OH groups are made to react with a silicone unit (e–1C) having the formula

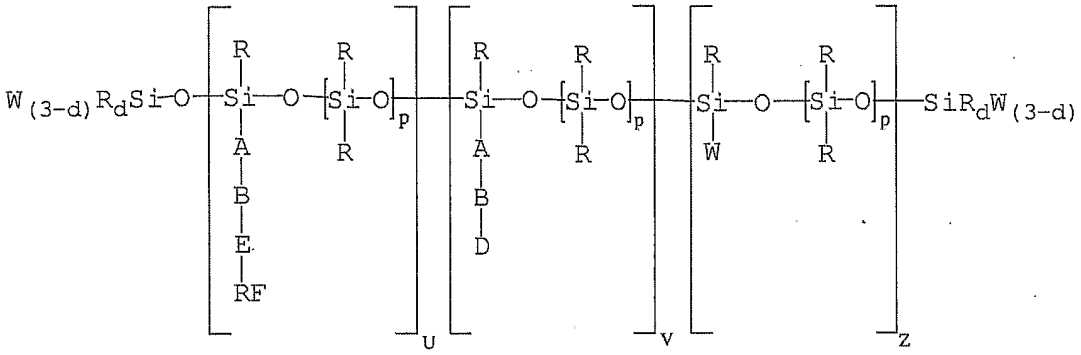
$$R^1\text{–}SiR_dH_{(3-d)}$$

where R^1 is chlorine, d is comprised between 0 and 3, and R is as defined above, said unit being present in a quantity comprised between 0.005 and 0.2 moles per mole of unit (a–1C).

The reaction can be followed by means of a spectrophotometric analysis until the –OH groups disappear completely.

A second class of ingredients of the composition of the invention is constituted by the POS2 compounds. POS2 designates two classes of fluorinated silicone polymers (respectively, POS2A and POS2B) that have, in the chain, alkenyl groups such as for example vinyl, allyl, butenyl, pentenyl groups, preferably vinyl groups and/or allyl groups.

A first class of compounds POS2 useful for the provision of the invention is constituted by the ones termed here POS2A. These compounds have the general formula (2A):

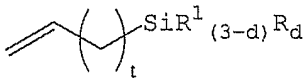


where:

W is a C_2–C_3 linear alkenyl group, vinyl or allyl, p, R, RF, A, B, D, E, u, v, z, p and d are as defined above.

A preferred POS2A polymer has a viscosity comprised between 100 and 300 cP.

In a further aspect, the invention relates to the synthesis of the POS2A compounds. The method is based on the use of a specific silicone unit (c–2A) having the formula



already encountered in an embodiment of the synthesis of the POS1B (to which reference is made for the definition of the variables), which is reacted according to two slightly different methods depending on whether the fluorinated portion is to be introduced before or after the synthesis of the

silicone skeleton of the polymer.

In a first embodiment a), the fluorinated portion of the POS2As is introduced before the synthesis of the silicone skeleton of the polymer. In this case, the synthesis of the POS2A compounds proceeds in a manner similar to the one described for the POS1B compounds: a first step of synthesis of the basic fluorinated monomer, a second step of polymerization of the monomers to form partial chains, a third step for forming the final silicone skeleton of the polymer and a fourth subsequent step for ending the polymerization with blocking of the –OH or –OR reactive groups.

In this embodiment, first of all the fluorinated monomer (a–2A), identical to the monomer (a–1B) prepared in relation to the synthesis of the POS1Bs, is prepared. The synthesis of (a–2A) occurs advantageously in the same manner described in relation to the preparation of (a–1B) in the synthesis of the POS1Bs.

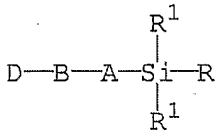
In the second step, partial chains of the POS2A polymer are formed by mixing:

– at least one silicone unit (c–2A) described previously, with

– the fluorinated monomer (a–2A) prepared above, and with

– at least one silicone unit (b–2A) identical to the unit (b–1B)

Optionally, but preferably, the mixture also receives the addition of a further monomer (d–2A) having the formula



identical to the unit (d–1B) and where R, R^1, A, B and D are defined as above. As in the other cases in which this residue is present, the epoxy group is meant to improve the adhesion of the fluorinated composition to the polymeric substrate to which it is applied.

For synthesis scheme a), for one mole of silicone unit (b–2A) it is possible to add 0.25 to 0.75 moles of fluorinated monomer (a–2A), 0.25 to

0.75 moles of silicone unit (c–2A) and 0 to 0.5 moles of silicone unit (d–2A).

It has been found that the ratio between the unit (c–2A) and the fluorinated monomer (a–2A) is important in order to achieve the ideal crosslinking of the product (which improves with a greater number of alkenyl groups) and the lowest surface tension (which decreases as the percentage of fluorine increases) in the final composition. The higher degree of crosslinking also entails a better anchoring of the polymer to the treated surface and a reduced migration of the final silicone film on the adhesive article once it is detached from the support. The low surface tension in fact favors the release of the silicone article from the support.

Step ii), when R^1 is chlorine, is advantageously performed in a stream of nitrogen in order to remove the hydrochloric acid that has formed and in a solvent preferably selected among toluene, hexane and heptane. The operating temperature is comprised between 30° and 80°C. The reaction time is comprised between 60 and 120 minutes. If R^1 is alkoxy, step ii) is advantageously performed in a solvent preferably selected among toluene, hexane and heptane, at 60°-130°C, in a stream of nitrogen in order to remove the alcohol that has formed.

The third step iii) comprises forming the final chains and the fourth step iv) comprises ending the polymerization.

The forming of the final chains occurs substantially by bringing the reaction mixture to a temperature comprised between 130°C and 150°C, at which the –OH groups and the –OR groups condense together.

If R^1 is chlorine, however, it is necessary to precede the third step iii) with a step of hydrolysis, so as to restore free –OH groups. This step can occur, for example, by washing the mixture with water, subsequently removing the HCl that has formed by means of further washes. The actual condensation step entails raising the organic reaction mass to the temperature of 130°C–150°C in the presence of a strong acid, preferably

trifluoroacetic acid, or of a base, such as strontium or barium hydroxide. This process can be performed in a stream of nitrogen in order to eliminate the water or ROH that forms in the reaction and continues until the preferred degree of viscosity is reached.

For synthesis scheme a), the reaction for polymerization of the –OH groups is interrupted by adding a total quantity comprised between 0.005 and 0.2 moles per mole of unit (b–2A) of at least one silicone unit selected between:

– a silicone unit (e–2A) $R^1—SiR_dW_{(3-d)}$

where the variables are defined as above (in particular d is comprised between 0 and 3).

The excess of the silicone unit (e–2A) can be easily removed for example by distillation. In this case also, as for the POS1Bs, it is preferable to thoroughly dehydrate the POS2A silicone polymer by distillation.

In a different embodiment b), the fluorinated portion of the POS2As is introduced after the synthesis of the silicone skeleton of the polymer. In this case, the first step comprises mixing:

– the silicone unit (c–2A) described above, with

– a silicone unit (b–2A), and

– at least one silicone unit (e–2A),

where the unit (c–2A) is present in excess with respect to the other units.

Optionally, but preferably, the mixture also receives the addition of a further monomer (d–2A) described above.

For synthesis scheme b), for one part of silicone unit (b–2A), it is possible to add between 0.5 and 1 mole of alkenyl silicone unit (c–2A), between 0 and 0.5 moles of silicone unit (d–2A), and between 0.05 and 0.15 total moles of silicone unit (e–2A).

Step b–1) is advantageously performed in a stream of nitrogen and in a solvent such as toluene, hexane, heptane. The operating temperature is comprised between 30° and 60°C. The reaction time is comprised between

60 and 120 minutes.

The larger quantity of unit (c–2A) that is present produces, at the end of this step, a silicone structure that has many alkenyl groups arranged along the chain. Moreover, by adding also the unit (e–2A), the chains that form are already the final ones of the skeleton of the polymer.

The second step b–ii) of the process comprises inserting a fluorinated residue in the silicone polymer. For this purpose it is preferable to wash beforehand the reaction mass several times with water in order to free it from traces of hydrochloric acid or alkyl acid produced during polymerization.

Advantageously, one continues (step b–ii) by adding to the alkenyl groups that are present, a iodofluorinated unit having the formula $C_nF_{2n+1}X$, where X can be –Cl, –Br or, preferably, –I. The moles of iodofluorinated unit are less than the moles of the W-group containing units so that the W groups that are present will not be totally saturated. Where d is other than 3, it is possible that some of the iodofluorinated units will react with the vinyl or allyl groups which are present at the ends of the polymer.

The reaction of addition at double bonds is performed advantageously in an atmosphere of nitrogen, at a temperature preferably comprised between 80° and 120°C, in the presence of a radical initiator, preferably AIBN, and optionally also of a reducing compound, preferably sodium metabisulfite. The sodium metabisulfite is advantageously in the form of a 20-30% aqueous solution.

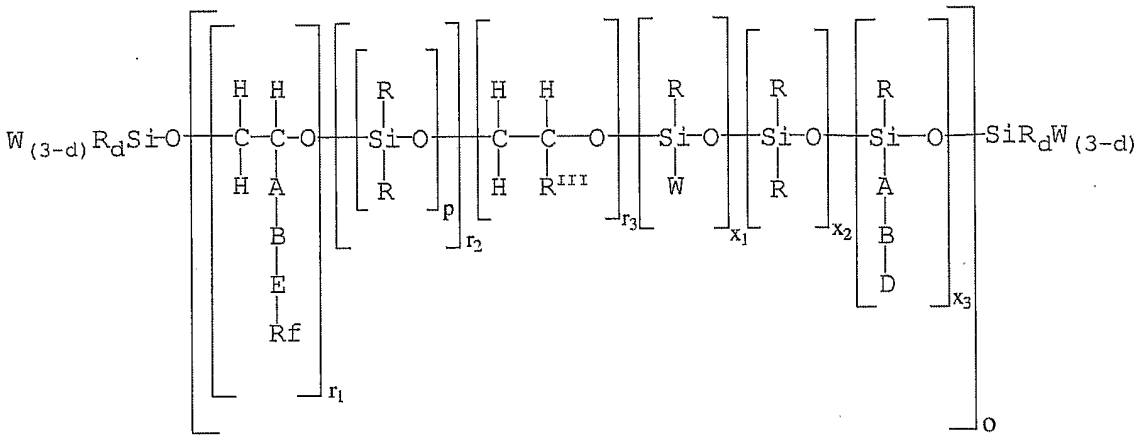
In order to eliminate the atom of X from the chain (step b–iii), it is possible to proceed according to two different methods, depending on the result that one prefers to obtain.

In a first embodiment (step b–iii–1), the fluorinated polymer of step b–ii) is treated with a strong base, preferably an alkaline metal hydroxide, more preferably sodium hydroxide, advantageously in solution, more preferably a 25-30% water-alcohol solution of sodium hydroxide. In this manner, a final fluorinated polymer is obtained that has a double bond in the

same position where it was before the radical attack of the fluorinated unit.

In a different embodiment (step b–iii–2), the fluorinated polymer is treated with a combination of a radical initiator, preferably AIBN, and a organic compound of tin, preferably butyl tin hydride, at a temperature advantageously comprised between 60° and 100°C, more preferably equal to 80°C. According to the method just described, the atom of X is replaced with an atom of H.

A second class of POS2 compounds useful for providing the invention is constituted by the ones termed here POS2B and having the general formula (2B):



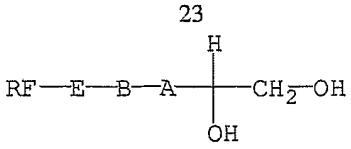
where:

r_1, r_2, r_3, x_1, x_2, x_3, o, W, R, RF, A, B, E, D and d are defined as for the POS1C compounds.

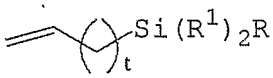
A preferred POS2B polymer has a viscosity comprised between 10 and 50cP.

In a further aspect, the invention relates to the synthesis of the POS2B compounds. The method substantially resembles the one already described for the preparation of the POS1Cs. The method comprises a first step of polymerization of the basic monomers in order to form the skeleton of the polymer and a second step for ending the polymerization.

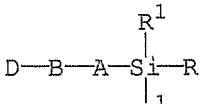
In a preferred embodiment, the first step comprises reacting a fluorinated glycol (a–2B) having the general formula:

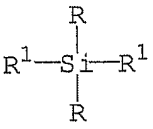


and identical to the glycol (a–1C), with at least one silicone unit (c–2B) having the formula



Optionally, but preferably, the mixture also receives the addition of a further monomer selected among:

– monomer (d–2B) having the formula 

– monomer (b–2B) identical to the unit (b–1C), 

– and mixtures thereof.

In the POS2B, R^1 is chlorine, while the variables are as defined above. The fluorinated glycol (a–2B) is used in any pure enantiomeric form or mixture of enantiomers. Moreover, in order to reduce the quantity of fluorine incorporated in the polymer, it is possible to optionally substitute part of the fluorinated glycol (a–2B) with a non-fluorinated silicone unit (b–1B) already described and/or a non-fluorinated glycol such as ethylene glycol, propylene glycol and hexanediol in a quantity comprised between 0 and 0.5 moles per mole of fluorinated glycol.

For one mole of added fluorinated glycol (a–2B), it is advantageous to use a quantity in moles of silicone unit (b–2B) comprised between 0 and 0.5, a quantity in moles of alkenyl silicone unit (c–2B) comprised between 0.25 and 1, and a quantity in moles of silicone unit (d–2B) comprised between 0 and 0.5.

Step i) is advantageously performed at between 30°C and 60°C, in a solvent such as a toluene, acetonitrile or t-butyl methyl ether in a stream of nitrogen. The reaction time varies between 60 and 180 minutes.

The second step is preceded by a further step of washing the reaction

mass with water in order to convert the remaining Si–R^1 groups into Si–OH groups and remove the hydrochloric acid that has formed. The Si–OH groups are then reacted (step ii) with at least one unit selected among:

– silicone unit (e–2B) having the formula R^1-$SiR_dW_{(3-d)}$ where d is an integer comprised between 0 and 3.

The reaction can be followed by spectrophotometric analysis until the –OH groups disappear completely.

The unit (e–2B) is added in a total quantity comprised between 0.005 and 0.2 moles per mole of unit (a–2B).

The fluorinated composition according to the invention also comprises one or more catalysts of the hydrosilylation reaction.

The reaction of addition of a Si–H group to a double bond is termed hydrosilylation reaction and is widely treated in the literature. It can occur for example by means of a radical mechanism initialized by ultraviolet light, organic peroxides such as t-butyl peroxide, AIBN, benzoyl peroxide or, finally, through metallic complexes, particularly of the transition metals. Catalysts based on platinum, palladium, salts of lead or of tin, such as stannous octoate or dibutyl tin di-acetate, are commonly used. Chloroplatinic acid is often chosen in these reactions, since it acts even if it is present in extremely small quantities (between 10^{-8} and 10^{-5} moles of catalyst per mole of hydrosilane). In the provision of the present invention, it has been found that any known catalyst is usable but it is particularly advantageous to resort to the complex formed by a chloroplatinic acid with vinylsiloxanes, preferably the complex of hexachloroplatinic acid with divinyltetramethyldisiloxane. This class of catalysts is described in US 3,419,593 and by J.L Speier in Adv. Organometal. Chem. 17 (1979) 407-447.

The quantity of hydrosilylation catalyst that is used in the invention is comprised between 0.01 and 1 part of platinum-based catalyst per 100 parts of combined mixture (POS1 + POS2). If the catalyst is a complex of

chloroplatinic acid, it is used in a quantity comprised between 1 and 500 parts by weight of platinum per million parts by weight of combined mixture (POS1 + POS2).

As mentioned, the fluorinated composition according to the invention can optionally comprise other ingredients, for example in order to stabilize the mixture of the basic components at ambient temperature. These ingredients are common in the field and are well-known to the person skilled in the art. Among the optional ingredients, mention can be made of organic compounds such as dialkyl maleate and dialkyl fumarates and the like. Preferably, bis(dimethoxyethyl)maleate is added in a quantity comprised between 0.5 and 10 parts by weight per 100 parts of combined mixture (POS1 + POS2).

The fluorinated silicone composition of the invention is particularly advantageous because thanks to the preparation methods and the orderly structure of its components (POS1 and POS2) it has chemical and physical properties that can be optimized according to the specific situation of use.

The characteristic of the fluorination of both polymers (POS1 and POS2) considerably improves their mutual mixing and the intimate contact between them, with a consequent increase in the performance of the composition. In particular, it has been found that the presence of fluorinated chains in both polymers is a considerable advantage if the final mixture is spread on the polymeric support without solvent.

In a further aspect, the present invention relates to a crosslinked composition, preferably in the form of a film, that can be obtained by applying heat to a composition as defined above.

The non-crosslinked composition as well as the crosslinked composition of the invention have a much lower surface tension per unit of surface than a normal silicone polymer. In this way, the effort for removing the adhesive article from a treated support is markedly lower than in known products without however reducing the anchoring efficiency of the support.

Finally, the fine control that is obtainable with the invention regarding the quantity of fluorine that can be incorporated in the composition (and therefore in the final crosslinked composition) is a considerable advantage also in terms of costs, because in view of the very high cost of the fluorinated monomer it is possible to optimize its quantity according to the intended reduction in surface tension.

In a further aspect, the present invention relates to a laminated element, particularly as a temporary support for adhesive films, comprising:
– a crosslinked composition such as the one described above, and
– a polymeric foundation material.

The laminated element can comprise one or more layers of a fluorinated silicone composition as defined above, applied to a foundation having a polymeric matrix. The polymeric foundation material is preferably selected from the group consisting of polyethylene terephthalate, polytetramethylene terephthalate, polyethylene 2,6-naphthalate, polyethylene-1,4-cyclohexylene, dimethylene terephthalate, polyethylene terephthalate/adipate, polyethylene terephthalate/sebacate, polypropylene, PVC, polyethylene and mixtures thereof.

In the method of preparation of the laminated element, the basic silicone components (preferably in the liquid state) POS1 and POS2 are kept separate until they are used. The POS2 is then mixed with the hydrosilylation catalyst and the various optional additives. Then the POS1 with the Si-H groups is added and the mixture thus prepared is applied to the polymeric foundation film, for example by means of an industrial device. This operation can be performed with or without the aid of a solvent that optimizes the viscosity of the silicone mass. If used, the solvent is advantageously selected among one or more of the following: toluene, t-butyl methyl ether, C4–C8 alkane, preferably hexane, heptane, octane, and mixtures thereof. Optionally, after each addition, especially after the additions of POS1 and POS2, it is preferable to perform additional mixing in

order to improve the uniform distribution of the ingredients.

The quantity of adhesive-releasing silicone composition to be applied to the polymeric film to be treated is comprised between 0.1 and 2 g/m^2, preferably between 0.3 and 1.2 g/m^2 for each layer, it being understood that it is possible to apply one or more layers.

Once the silicone mixture has been applied to the polymeric support, it is advantageous to apply heat with ordinary heating means so as to facilitate the crosslinking of said mixture. In particular, the Si-H groups (POS1) start to react with the Si–[...]–$CH=CH_2$ groups (POS2), a process which is facilitated by the presence of an appropriate catalyst and is accelerated by bringing the composite support formed by polymer plus adhesive silicone mixture to a temperature of approximately 120°–200°C.

The application of heat advantageously lasts between 10 seconds and 5 minutes, so as to obtain a solid film that is perfectly anchored to the substrate.

The laminated element thus provided is particularly adapted to be used as a support for the temporary adhesion of adhesive articles such as labels and adhesive tapes. The composite substrate in fact releases the applied articles with minimal effort and without transferring the thin layer of fluorinated silicone to the adhesive article (so-called "migration").

In a further aspect, the present invention relates to the products obtainable by the synthetic methods that are disclosed above.

Other characteristics and advantages of the present invention will become better apparent from the description of the following preferred embodiments, intended exclusively as non-limiting examples.

In a similar manner, although the examples that follow as well as the text explicitly describe only some preferred embodiments of the invention, it is immediately evident to the person skilled in the art that many variations to the individual described aspects are possible without thereby abandoning the scope of the inventive concept.

In the description of the examples that follows,

– Examples 1-5 relate to the synthesis of POS1A compounds,

– Examples 6-8 relate to the synthesis of POS1B compounds,

– Examples 9-10 relate to the synthesis of POS1C compounds,

– Examples 11-19 relate to the synthesis of POS2A compounds,

– Examples 20-22 relate to the synthesis of POS2B compounds, and

– Examples 23-30 relate to the synthesis of the final fluorinated polymer constituted by POS1 compounds bound to POS2 compounds.

In the examples that follow, if reference is made to a mixture of fluorinated compounds of various chemical kinds (alcohols, alkenes and others), one intends a mixture of derivatives identified in each instance by means of the average molecular weight and in which the fluorinated portion has the general formula C_nF_{2n+1}– and n takes the values 8, 10, 12, 14, 16. More precisely, the fluorinated portion of the mixture has the following composition:

C_8F_{17}–	65.90%
$C_{10}F_{21}$–	22.96%
$C_{12}F_{25}$–	7.03%
$C_{14}F_{29}$–	3.03%
$C_{16}F_{33}$–	1.08%

Example 1

A round-bottomed four-neck 500-ml flask, provided with a thermometer, a mechanical agitator, a countercurrent condenser and a dropping funnel for loading, is mounted on a heating oil bath. 73.5 g (0.0324 moles) of polymethylhydrosiloxane (Aldrich^R) and 0.7 g of t-butylperoxide are then loaded. In an atmosphere of nitrogen, the reaction mixture is brought to 150°C and at this temperature the dropping of 85.8 g (0.173 moles) of a mixture of olefins having the formula $C_nF_{2n+1}CH=CH_2$ and an average MW of 496 g/mole begins, continuing the dripping for one hour.

Once dripping has ended, the temperature is maintained for two more hours so as to leave the reaction to continue autonomously.

159 g of perfectly clear fluorinated silicone polymer with a viscosity equal to 190-200 cP are obtained. The viscosity measurements were performed by using a Brookfield DV–E^R viscometer.

Example 2

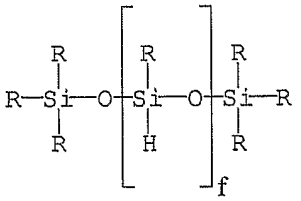
According to the same procedure described in Example 1, the reaction is repeated, but by using 88.2 g of a mixture of olefins having the formula $C_nF_{2n+1}CH_2CH=CH_2$ and an average MW equal to 510 g/mole. The final polymer showed a viscosity of 210–230 cP.

Example 3

In the same apparatus described in Example 1, 73.5 g of polymethylhydrosiloxane (Aldrich^R) are loaded. In an atmosphere of nitrogen, 0.7 g of t-butylperoxide are loaded and the reaction mixture is brought to 150°C. A this temperature, 42.6 g (0.086 moles) of a first mixture of olefins having the formula $C_nF_{2n+1}CH=CH_2$ and an average MW equal to 496g/mole, and 43.8 g (0.086 moles) of a second mixture of olefins having the formula $C_nF_{2n+1}CH_2CH=CH_2$ with MW = 510g/mole are dripped over one hour. After dripping, the reaction is allowed for two more hours at the same temperature. In this manner 159 g of a perfectly clear fluorinated silicone polymer are obtained.

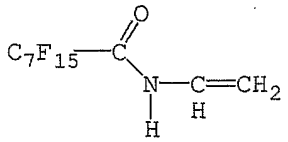
Example 4

In the same apparatus described in Example 1, 13 g (0.0057 moles) of polymethylhydrosiloxane having the formula (f approximately 35):



and 0.01 g of t-butylperoxide are loaded. The reaction mixture is brought to 150°C and in an atmosphere of nitrogen one begins to drip 12.60 g (0.028

moles) of fluorinated amide having the formula



At the end of the dripping, the reaction is allowed to continue at 150°C for 4 more hours, checking by gas chromatography for the total disappearance of the fluorinated amide. One obtains 25 g of yellow fluorinated polymer, which is diluted to 70% with toluene, obtaining a polymer with a viscosity of 190-195 cP.

Example 5

(a) Synthesis of the fluorinated olefin having the formula:

$$C_nF_{2n+1}CH_2–CH_2–O–CH_2–CH=CH_2$$

In an apparatus constituted by a round-bottomed four-neck 250-ml flask provided with thermometer, mechanical agitator, coolant in countercurrent and drip funnel for loading, 51.4 g of fluorinated alcohol having the formula $C_nF_{2n+1}CH_2CH_2OH$ (0.1 moles), 38.3 g (0.5 moles) of allyl chloride, 100 ml of a 50% aqueous solution of KOH, 3.64 g (0.01 moles) of hexadecyltrimethylammonium bromide are introduced. The temperature of the mixture is brought to 42°C and, in an atmosphere of nitrogen, the reaction is allowed to continue for 6 hours.

At the end of the reaction, the mixture is diluted with 100 ml of methylene chloride and washed several times with water. The solvent is then eliminated from the mixture by distillation, recovering 50.4 g of product with a yield of 91%.

b) Synthesis of the fluorinated polymer

In the same apparatus described in Example 1, 40 g of polymethylhydrosiloxane (Aldrich^R) are loaded. In an atmosphere of nitrogen, 0.4 g of t-butylperoxide are then loaded, and the reaction mixture is brought to 150°C. At this temperature, the dripping of 48.7 g (0.088 moles) of the olefin synthesized in step (a) begins (and continues for one hour).

Once dripping has ended, the reaction is continued for two more hours at the same temperature. 89 g of pale yellow fluorinated silicone polymer, with a viscosity of approximately 330 cP are thus obtained.

Example 6

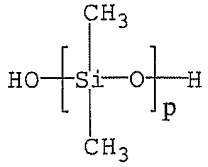
a) Synthesis of the fluorinated monomer having the formula:

$$C_nF_{2n+1}CH_2CH_2Si(Cl)_2CH_3$$

In an apparatus identical to the one described in Example 1, 49.6 g (0.1 moles) of a mixture of olefins having the formula $C_nF_{2n+1}CH=CH_2$ and an average MW 496g/mole and 0.5 g of a 30% solution in 2-propanol of chloroplatinic acid are added. The reaction mixture is brought to 60°C and in an atmosphere of nitrogen, the dripping of 13.8 g (0.12 moles) of dichloromethylsilane (formula $CH_3(Cl)_2SiH$) begins. Dripping is continued for one hour and once dripping has ended, the reaction is continued until the fluorinated olefin disappears. Distillation is performed in vacuum in order to remove the excess dichloromethylsilane.

b) Synthesis of the polymer

In a round-bottomed four-neck flask as described in Example 1, 110 g (0.2 moles) of a silicone polymer having the formula



with p approximately equal to 7, having a MW=550 g/gmole, and 70 g of n-hexane are added. The temperature of the mixture is brought to 40-45°C and the dripping of a mixture of 61.1 g (0.1 moles) of the silicone monomer of Example 6(a) and of 11.5 g (0.1 moles) of dichloromethylsilane begins. The dripping continues for one hour. At the end of the dripping, a gentle stream of nitrogen is made to flow within the reaction mass in order to remove the hydrochloric acid that has formed. After two hours of reaction, the organic mass is washed several times with water until a neutral pH is reached. After separation from the aqueous phase, the organic phase receives the addition

of 0.8 g of trifluoroacetic acid, which acts as a catalyst for the condensation of the –OH groups formed in the polymer during washing with water. The organic mixture is placed in the same round-bottomed reaction flask as in Example 1, in which a Claisen cooling system is also mounted. Distillation of the solvent begins and heating is continued until 140°C are reached. During this step, a gentle stream of nitrogen is made to flow in the reaction mass, allowing to remove more easily the solvent and the water that forms during the condensation of the –OH groups.

Any Si–OH groups remaining at the end of this step are eliminated by reacting them with chlorodimethylsilane. This operation is followed by IR analysis.

A uniform white silicone polymer with a viscosity equal to 95 cP is thus obtained.

Example 7

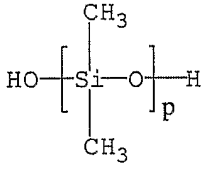
a) Synthesis of the monomer having the formula

$$C_nF_{2n+1}\ CH_2–CH_2–O–CH_2–CH_2–CH_2–Si(Cl)_2CH_3$$

55.4 g (0.1 moles) of product obtained in Example 5(a) receive the addition of 0.5 g of a 30% solution in 2-propanol of chloroplatinic acid. The reaction mixture is brought to 60°C and the dripping of 13.8 g (0.12 moles) of dichloromethylsilane begins. The dripping lasts one hour. After this, the reaction is allowed to continue until the fluorinated olefin disappears. Finally, the excess of dichloromethylsilane is distilled.

b) Synthesis of the polymer

In a round-bottomed four-neck flask as described in Example 1, 99 g (0.18 moles) of a silicone polymer having the formula:



with p equal to approximately 7 having a MW=550 g/gmole, are added. The temperature of the organic mixture is brought to 40-45°C and the dripping of

a mixture of 60.2 g (0.09 moles) of silicone monomer described in Example 7(a) and of 10.3 g (0.09 moles) of dichloromethylsilane begins. The dripping continues for one hour. At the end of the dripping, a gentle stream of nitrogen is made to flow within the reaction mass in order to remove the hydrochloric acid that has formed. After two hours of reaction, the organic mass is washed several times with water until a neutral pH is obtained.

After separation from the aqueous phase, the organic phase receives the addition of 0.74 g of trifluoroacetic acid.

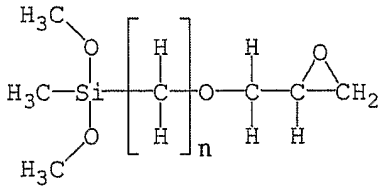
The organic mixture is placed in the same round-bottomed reaction flask of Example 1, in which a Claisen cooling system is also mounted. Distillation of the solvent begins and then heating is continued until 130-140°C are reached. During this step, a gentle stream of nitrogen is made to flow within the reaction mass and allows to remove more easily the solvent and the water that forms during the condensation of the –OH groups.

Any Si–OH groups formed during washing are eliminated by making them react with chlorodimethylsilane. This operation is followed by means of IR analysis.

A pale yellow homogeneous silicone polymer with a viscosity of 110 cP is thus obtained.

Example 8

a) Synthesis of the monomer having the formula



with n=3

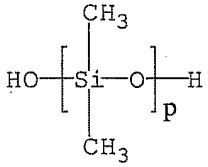
In an apparatus constituted by a 250-ml four-neck round-bottomed flask provided with a thermometer, a mechanical agitator, a coolant in countercurrent and a drip funnel for loading, 80 g of allylglycidylether (0.7 moles) and 0.5 g of a 30% solution in 2-propanol of chloroplatinic acid are

introduced.

The reaction mixture is brought to 60°C and the dripping of 89.2 g (0.84 moles) of methyldimethoxysilane begins. The dripping lasts one hour, after which the reaction is allowed to continue until the fluorinated olefin disappears. Finally, the excess of methyldimethoxysilane is distilled, obtaining 143.4 g of addition product (93% yield).

b) Synthesis of the polymer

In a round-bottomed 500-ml four-neck flask as described in Example 1, 99 g (0.18 moles) of a silicone polymer having the formula



with p approximately equal to 7, having a MW=550 g/gmole, and one gram of stannous octoate are added. The temperature of the organic mixture is brought to 60-65°C and the dripping begins of a mixture of 9.91 g (0.045 moles) of the silicone monomer described in Example 8(a), 27.1 g (0.045 moles) of the silicone monomer synthesized in Example 6(a), where the Cl–groups are substituted with methoxy groups, and 9.56 g (0.09 moles) of methyldimethoxysilane. The dripping continues for thirty minutes. At the end of the dripping, a gentle stream of nitrogen is made to flow within the reaction mass in order to remove the methyl alcohol that has formed. The temperature is raised gradually to 130-140°C and remains at this value for two hours.

Any Si–OH groups in excess are made to react by adding dimethylmethoxysilane to the organic mass.

The disappearance of the –OH groups is followed by means of IR analysis. The excess of dimethylmethoxysilane is distilled. The final polymer has a viscosity of 105 cP.

Example 9

In a 1000-ml reactor completed as described in Example 1, 152.3 g

(0.28 moles) of fluorinated glycol having the general formula $C_nF_{2n+1}CH_2CH(OH)CH_2OH$ and an average MW equal to 544 g/gmole are added.

Once the temperature has been brought to 50°C, the dripping of a mixture formed by 16.1 g (0.14 moles) of dichloromethylsilane and 18.0 g (0.14 moles) of dichlorodimethylsilane begins.

The dripping is continued for 1.5 hours, at the end of which the components of the mixture are left to react for two more hours with a gentle stream of nitrogen in order to remove the hydrochloric acid that gradually forms.

At the end, the organic mass is dissolved in 150 cc of t-butyl methyl ether and repeated washing with deionized water is performed until a neutral pH is obtained.

The Si–OH groups that may have formed due to the reaction of the Si–Cl terminals with the water are made to react by adding dimethylchlorosilane to the organic mixture.

This last step is followed by means of IR spectrophotometric analysis up to the complete disappearance of the Si–OH groups. Finally, the ether is distilled together with any excess of dimethylchlorosilane. The viscosity of the polymer is approximately 15-20 cP.

Example 10

In an apparatus as in the preceding example, the following are added:

– 152.3 g (0.28 moles) of fluorinated glycol having the formula $C_nF_{2n+1}CH_2CH(OH)CH_2OH$,

– 110 g (0.2 moles) of the silicone polymer described in Examples 6 (b), 7 (b), and 8 (b) with average MW equal to 550 g/mole, and

– 220 g of t-butyl methyl ether.

The reaction mixture is brought to 50°C and the dripping begins of:

– 27.6 g (0.24 moles) of dichloromethylsilane, and

– 31.0 g (0.24 moles) of dichlorodimethylsilane.

One then continues as described in Example 9, but leaving approximately 3-5% ether so as to make the product more uniform and stable.

Example 11

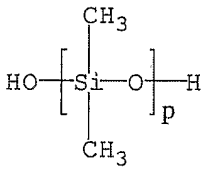
a) Production of the fluorinated monomer having the formula

$$C_nF_{2n+1}CH_2CH_2Si(Cl)_2CH_3$$

As described in Example 6(a)

b) Synthesis of the polymer

In a round-bottomed four-neck flask provided with the same instruments as described in Example 1, 110 g (0.2 moles) of a silicone polymer having the formula



where p is approximately 7, having a MW=550 g/gmole, and 200 g of n-hexane are added. The temperature of the organic mixture is brought to 55-60°C and the dripping of a mixture of 61.1 g (0.1 moles) of the silicone monomer prepared in the preceding step and of 14.1 g (0.1 moles) of dichloromethylvinylsilane begins. The dripping continues for one hour. At the end of the dripping, a gentle stream of nitrogen is made to flow within the reaction mass in order to remove the hydrochloric acid that forms. After two hours of reaction, the organic mass is washed several times with water until a neutral pH is obtained. The phases are separated and the organic phase is collected. 1.1 g of trifluoroacetic acid are added and distillation of the solvent begins by passing a gentle stream of nitrogen through the organic mass. The Si–OH groups present in the polymer can condense together, increasing the viscosity of the polymer. Even at the end of the distillation, the polymer is still kept under agitation for three hours, increasing gradually the temperature up to 140°C. The viscosity of the polymer gradually increases, but it is possible to block it at the most appropriate moment by

adding to the organic mixture dimethylchlorosilane, so as to react the Si–OH groups that are still present in the polymer, making them incapable of condensing further.

A homogeneous white silicone polymer with a viscosity of approximately 150 cP is obtained.

Example 12

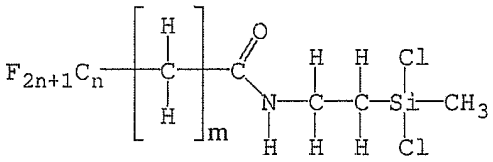
The procedure of Example 11 is repeated, except for the fact that one uses 62.5 g (0.1 moles) of a fluorinated monomer which is different from the one previously synthesized in step (a), having the formula

$$C_nF_{2n+1}CH_2\ CH_2\ CH_2Si(Cl)_2CH_3$$

In this case also, one obtains a clear silicone polymer with the same viscosity as the one obtained in Example 11.

Example 13

The procedure of Example 11 is repeated, except for the fact that one uses 69.5 g (0.1 moles) of a different fluorinated monomer having the formula



where m is 3, obtaining a yellow silicone polymer with a viscosity equal to 180 cP.

Example 14

In a round-bottomed four-neck 1000-ml flask provided with the same instruments described in Example 1, one adds 165 g (0.3 moles) of the silicone polymer of Example 11(b), with p approximately equal to 7, having a MW=550 g/gmole, and 300 g of n-hexane. The temperature of the organic mixture is brought to 60–65°C and the dripping begins of a mixture of 61.1 g (0.1 moles) of the silicone monomer described in Example 6(a), 62.5 g (0.1 moles) of the fluorinated silicone monomer described in the preceding example, and 14.1 g (0.1 moles) of dichloromethylvinylsilane. The mixture

of monomers is dripped for 1.5 hours. At the end of the dripping, a gentle stream of nitrogen is passed through the reaction mass in order to remove the hydrochloric acid that forms. After two hours of reaction, the organic mass is washed several times with water until a neutral pH is obtained. The phases are separated and the organic phase is collected. 1.7 g of trifluoroacetic acid are added and distillation of the solvent begins by passing a gentle stream of nitrogen through the organic mass. At the end of the distillation, the polymer is kept under agitation for three hours, gradually increasing the temperature to 130°C. The viscosity of the polymer increases gradually, but can be blocked at will by adding dimethylchlorosilane to the organic mixture in order to react the Si–OH groups that are still present in the polymer, making them incapable of further polymerization.

A pale yellow homogeneous silicone polymer with a viscosity set to 160-170 cP is obtained.

Example 15

In a round-bottomed four-neck 1000-ml flask provided with the same instruments described in Example 1, one adds 165 g (0.3 moles) of the silicone polymer of Example 14, with p approximately equal to 7, having a MW=550 g/gmole, and 1.6 g of stannous octoate. The temperature of the organic mixture is brought to 60-65°C and the dripping begins of a mixture of 60.2 g (0.1 moles) of the silicone monomer described in Example 6(a), where both the –Cl are substituted by the $-OCH_3$ groups, 22.0 g (0.1 moles) of epoxy silicone monomer described in Example 8(a), and 13.2 g (0.1 moles) of vinylmethyldimethoxysilane. The mixture of monomers is dripped for thirty minutes. At the end of the dripping, a gentle stream of nitrogen is passed through the reaction mass in order to remove the methyl alcohol that forms. The polymer is kept under agitation for three hours, gradually increasing the temperature up to 120°C. Vinyldimethylmethoxysilane is added to the organic mixture in order to react the Si–OH groups that are still present in the polymer, blocking their polymerization.

A homogeneous white silicone polymer is obtained.

Example 16

In a 250-ml round-bottomed four-neck flask provided with the same instruments described in Example 1, one adds 40.4 g (0.073 moles) of the silicone polymer of Example 15, with p approximately equal to 7, having a MW=550 g/gmole, and 30 g of toluene. The temperature of the organic mixture is brought to 60–65°C and the dripping begins of a mixture of 0.88 g (0.0073 moles) of chlorodimethylvinylsilane and 9.84 g (0.07 moles) of dichloromethylvinylsilane. The mixture of monomers is dripped for 30 minutes. At the end of the dripping, a gentle stream of nitrogen is passed through the reaction mass in order to remove the hydrochloric acid that forms. After two hours of reaction, the organic mass is washed several times with water until a neutral pH is obtained. The organic phase is separated and collected, placing it in the same round-bottomed flask. One adds 30.4 g (0.051 moles) of a mixture of iodided compounds having the general formula $C_nF_{2n+1}I$, with medium equal to 9 and having a MW equal to 596 g, 0.1 g of the radical initiator AIBN, and 25 g of a 25% aqueous solution of sodium metabisulfite. The temperature of 80°C is maintained for 12-14 hours adding every two hours 0.1 g of AIBN. After the mixture of iodided compounds has disappeared completely, a solution of 3.08 g (0.077 moles) of NaOH in 7.4 g of ethanol and 1.8 g of water is added drop by drop. This last step of the process continues for 1.5 hours, at the end of which the organic phase is separated from the aqueous phase and the solvent is removed by distillation. A yellow silicone polymer with a viscosity of 198 cP is obtained.

Example 17

In a 250-ml round-bottomed four-neck flask provided with the same instruments described in Example 1, one adds 40.4 g (0.073 moles) of the dihydroxy silicone polymer of Example 16, with p equal to 7, having a MW=550 g/gmole, and 30 g of toluene. The temperature of the organic

mixture is brought to 60-65°C and the dripping begins of a mixture of 0.88 g (0.0073 moles) of chlorodimethylvinylsilane and 9.84 g (0.07 moles) of dichloromethylvinylsilane. The mixture of monomers is dripped for 30 minutes. At the end of the dripping, a gentle stream of nitrogen is passed through the reaction mass in order to remove the hydrochloric acid that forms. After two hours of reaction, one adds 18.55 g (0.035 moles) of a mixture of fluorinated thiols having the general formula $C_nF_{2n+1}CH_2CH_2SH$, (in which the values of n were given earlier) and 0.1 gr of radical initiator AIBN. The temperature of 80°C is maintained for 3-4 hours. After the fluorinated thiols have reacted completely, the organic part is washed several times with water until a silicone polymer having a neutral pH with a viscosity of 140–159 cP is obtained.

Example 18

a) Synthesis of the fluorinated silicone monomer having the formula

$$C_nF_{2n+1}CH_2CH_2SCH_2CH_2Si(Cl)_2CH_3$$

In a 250-ml round-bottomed flask provided with mechanical agitator, coolant in countercurrent, thermometer, drip funnel and thermostatically-controlled bath, 53.0 g (0.1 moles) of a fluorinated thiol having the formula $C_nF_{2n+1}CH_2CH_2SH$ and 0.1 g of radical initiator AIBN are added. In an atmosphere of nitrogen and at 75-80°C, one begins to slowly drip 15.5 g (0.11 moles) of dichloromethylvinylsilane, monitoring the temperature increase and interrupting the heating if necessary. The reaction is completed after two hours.

(b) Synthesis of the polymer

In a 500-ml round-bottomed four-neck flask provided with the same instruments described in Example 1, one adds 110 g (0.2 moles) of the dihydroxy silicone polymer of Example 17, where p is approximately 7, having a MW=550 g/gmole, and 200 g of n-hexane. The temperature of the organic mixture is brought to 60-65°C and the dripping of a mixture of 67.1 g (0.1 moles) of silicone monomer prepared in the preceding step, and of

14.1 g (0.1 moles) of dichloromethylvinylsilane begins. The mixture of monomers is dripped for 1.5 hours. At the end of the dripping, a gentle stream of nitrogen is passed through the reaction mass in order to remove the hydrochloric acid that forms. After two hours of reaction, the organic mass is washed several times with water until a neutral pH is obtained. The organic phase is separated and collected. 1.1 g of trifluoroacetic acid are added and distillation of the solvent begins. At the end of the distillation, the polymer is kept under agitation for three hours, gradually increasing the temperature to 130°C. The viscosity of the polymer gradually increases, but is blocked at the most appropriate moment by adding dimethylchlorosilane to the organic mixture until the Si–OH groups still present in the polymer disappear completely.

A homogeneous amber yellow silicone polymer is obtained.

Example 19

In a 1000-ml round-bottomed four-neck flask provided with the same instruments described in Example 1, 165 g (0.3 moles) of the dihydroxy silicone polymer of Example 18, where p is approximately 7, having a MW=550 g/gmole and 1.6 g of stannous octoate are added. The temperature of the organic mixture is brought to 60°-65°C and the dripping begins of a mixture of

66.2 g (0.1 moles) of the silicone monomer prepared in Example 18(a), where the –Cl groups have been substituted beforehand with methoxy groups with a simple reaction with methanol,

22.0 g (0.1 moles) of the epoxy silicone monomer of Example 8(a) and

13.2 g (0.1 moles) of vinylmethyldimethoxysilane.

The mixture of monomers is dripped for thirty minutes. At the end of the dripping, a gentle stream of nitrogen is passed through the reaction mass in order to remove the methyl alcohol that forms. The polymer is kept under agitation for three hours, gradually increasing the temperature up to 120°C.

If IR analysis shows the presence of still unreacted –OH groups, vinyldimethylmethoxysilane is added to the organic mixture until complete disappearance of the –OH groups occurs.

A homogeneous amber yellow silicone polymer with a viscosity of 135–136 cP is obtained.

Example 20

In a round-bottomed 1000-ml flask as in Example 1, 152.3 g (0.28 moles) of fluorinated glycol having the general formula $C_nF_{2n+1}CH_2CH(OH)CH_2OH$, with an average MW of 544 g/gmole are introduced.

After bringing the temperature to 50°C, the dripping begins of a mixture formed by 19.7 g (0.14 moles) of dichloromethylvinylsilane and 18.0 g (0.14 moles) of dichlorodimethylsilane.

The dripping is continued for 1.5 hours, at the end of which the components of the mixture are left to react for two more hours with a gentle stream of nitrogen in order to remove the hydrochloric acid that gradually forms.

At the end of the two hours, the mass is dissolved in 150 cc of t-butyl methyl ether and washed repeatedly with deionized water until a neutral pH is obtained.

The Si–OH groups that may have formed due to the reaction of the Si–Cl terminals with the water are reacted by adding chlorodimethylvinylsilane. This last step is followed by means of IR spectrophotometric analysis until complete disappearance of the Si–OH groups occurs. Finally, the ether is distilled together with any excess of chlorodimethylvinylsilane. The viscosity of the final polymer is equal to 10–12 cP.

Example 21

In a round-bottomed 1000-ml flask as in Example 1, 108.8 g (0.2 moles) of fluorinated glycol having the general formula

$C_nF_{2n+1}CH_2CH(OH)CH_2OH$, with an average MW of 544 g/mole, and 7.6 g (0.1 moles) of propylene glycol are introduced.

After bringing the temperature to 60°C, the dripping begins of a mixture formed by 21.1 g (0.15 moles) of dichloromethylvinylsilane and 19.2 g (0.15 moles) of dichlorodimethylsilane.

The dripping is continued for 1.5 hours, at the end of which the reaction of the components of the mixture is allowed to continue for two more hours with a gentle stream of nitrogen in order to remove the hydrochloric acid that gradually forms.

At the end of the two hours, the organic mass is dissolved in 160 cc of t-butyl methyl ether and washed repeatedly with deionized water until a neutral pH is obtained.

The Si–OH groups that may have formed due to the reaction of the Si–Cl terminals with the water are made to react by adding chlorodimethylvinylsilane. This last step is followed by means of IR spectrophotometric analysis until complete disappearance of the Si–OH groups occurs. Finally, the ether is distilled together with any excess of chlorodimethylvinylsilane. A pale yellow final product with a viscosity of 14–15 cP is obtained.

Example 22

In a 1000-ml reactor as in Example 1, one introduces 108.8 g (0.2 moles) of fluorinated glycol having the general formula $C_nF_{2n+1}CH_2CH(OH)CH_2OH$, with an average MW of 544g/mole, 55.0 g (0.1 moles) of a dihydroxy silicone polymer of Example 18, where p is approximately 7, having an average molecular weight of 550g/mole, and 150 g of t-butyl methyl ether.

After bringing the temperature to 50°C, the dripping begins of a mixture formed by 21.1 g (0.15 moles) of dichloromethylvinylsilane and 19.2 g (0.15 moles) of dichlorodimethylsilane.

The dripping is continued for 1.5 hours, at the end of which the

reaction of the components of the mixture is allowed to continue for two more hours with a gentle stream of nitrogen in order to remove the hydrochloric acid that gradually forms. At the end of the two hours, the organic phase is washed repeatedly with deionized water until a neutral pH is obtained.

The Si–OH groups that may have formed due to the reaction of the Si–Cl terminals with the water are made to react by adding chlorodimethylvinylsilane. Finally, the ether is distilled together with any excess of chlorodimethylvinylsilane. The viscosity of the product is 25-30 cP.

Examples 23–30

The following table lists some examples related to the reactions performed with various mixtures of the silicone polymers of the POS1 and POS2 types prepared earlier. The two types of polymers were mixed together in a suitable solvent that dissolves them both, further introducing in the mixture a catalyst of the hydrosilylation reaction, and an additive (also known as inhibitor) capable of keeping said mixture stable at ambient temperature.

The catalyst used is the platinum–divinyltetramethyldisiloxane complex with 3-3.5% platinum (purchased from ABCR GmbH & CO^{R}). The inhibitor used is bis–(methoxyethyl)maleate. Part of the solution obtained from the individual reactions was then spread on a common polymeric film and placed in a stove at 130-140°C for 3-4 minutes. At the end of this period, the surface tension of the treated surface (expressed as [mN/m]) was measured with the Owens-Wendt method.

POS1	POS2	Cat.	Inhib.	Solvent	[mN/m]
5 g POS1B ex.8	100 g POS2A ex.11	0.02 g	0.52 g	945 g, octane	17.34
10 g POS1B ex.6	90 g POS2A ex.9	0.02 g	0.52 g	945 g, heptane	18.47
5 g POS1A ex.1	100 g POS2A ex.11	0.02 g	0.52 g	945 g, heptane	15.03

POS1	POS2	Cat.	Inhib.	Solvent	[mN/m]
5 g POS1A ex.2	100 g POS2A ex.12	0.02 g	0.52 g	945 g, heptane	12.49
5 g POS1A ex.1	100 g POS2A ex.16	0.02 g	0.52 g	945 g, heptane	15.60
20 g POS1C ex.10	80 g POS2A ex.18	0.02 g	0.52 g	300 g, toluene	17.25
50 g POS1B ex.7	100 g POS2B ex.20	0.03 g	0.80 g	450 g, toluene	14.30
50 g POS1C ex.10	50 g POS2B ex.21	0.02 g	0.50 g	300 g, toluene	14.50

The disclosures in Italian Patent Application No. MI2004A001460 from which this application claims priority are incorporated herein by reference.

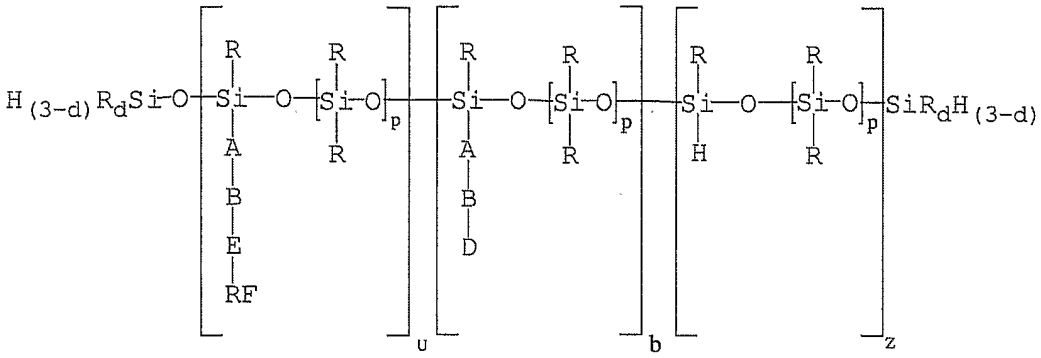
CLAIMS

1. A compound selected from the group consisting of:

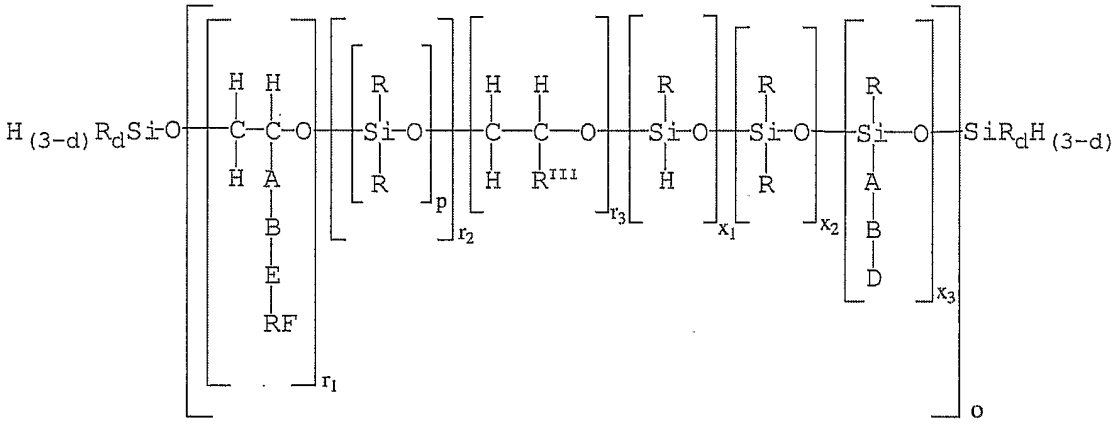
– compounds POS1A having the general formula (1A):

$$(R')(R)_2Si–O–[(H)_{1-k}(Z_1)_kSi(R)O–]_{f1}–[(H)_{1-y}(Z_2)_ySi(R)O–]_{f2}–Si(R)_2(R')$$

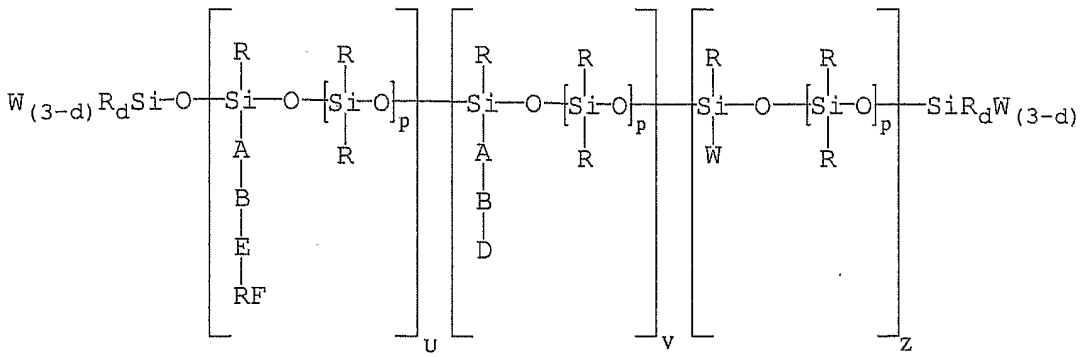
– compounds POS1B having the general formula (1B):



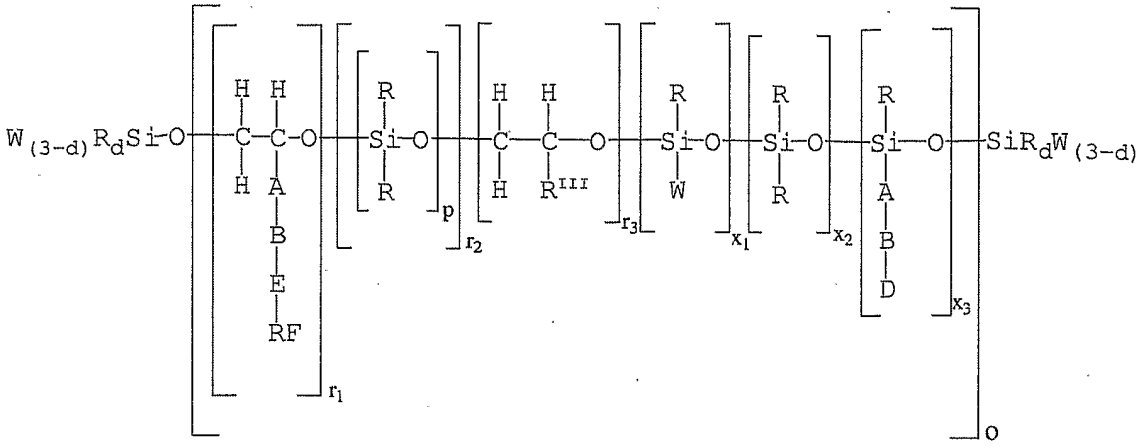
– compounds POS1C having the general formula (1C):



– compounds POS2A having the general formula (2A):



– compounds POS2B having the general formula (2B):



where for POS1A compounds:

R is C1–C10 alkyl, preferably C1–C3 alkyl, more preferably methyl or ethyl;

R' is R or hydrogen,

f_1 is a whole number comprised between 1 and 200;

f_2 is a whole number comprised between 0 and 100;

k is 0 or 1 where if f_1 is 1, k is 1,

if f_1 is 2, k is 1 in at least one repetition of the monomer f_1,

if f_1 is comprised between 3 and 200, in each repetition of the monomer f_1, k is independently 0 or 1, assuming that k is 1 in at least one monomer f_1,

y is 0 or 1,

A is selected from the group consisting of:

i) –CH=CH–,

ii) $-C_2H_4-$,

iii) $-C_3H_6-$,

iv) $-(CH_2)_q-$, where q is a whole number comprised between 1 and 9;

v) $-CH(CH_3)CH_2-$ bound to the silicon by means of the right end, and

vi) $-CH(CH_2CH3)CH_2-$ bound to the silicon by means of the right end;

B is absent or selected from the group consisting of –O–, –S–, and –NH–;

E is absent or is selected from the group consisting of

i) $-CH_2CH_2-$,

ii) –CH=CH–,

iii) $-CH=CH-CH_2-$,

iv) $-CH_2CH_2CH_2-$,

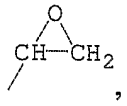
v) $-CH_2CH(OCH_3)CH_2-$,

vi) $-(CH_2)_m C(O)-$, bound to B by means of the right end and m is a whole number comprised between 0 and 10;

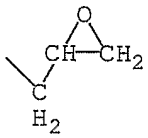
vii) $-(CH_2)_v-O-C(O)-$, v is a whole number comprised between 2 and 18;

Z_1 is a –A–B–E–RF group, where RF is a group $C_nF_{2n+1}-$ in which n is a whole number comprised between 2 and 20, preferably between 6 and 16, more preferably RF is a group C4–C18 perfluoroalkyl;

Z_2 is a –A–B–D group, where D is an epoxy group selected between:

ethylene oxide  ,

and

propylene oxide 

assuming that y, k and R' are such that there are at least two Si-H groups per POS1A molecule;

for POS1B compounds:

R, RF, A, B, E and D are defined as above;

d is any integer comprised between 0 and 3 unless otherwise indicated;

u is a whole number comprised between 1 and 400, preferably comprised between 10 and 200;

b is a whole number comprised between 0 and 400;

z is a whole number comprised between 2 and 400, preferably comprised between 10 and 200;

p is a whole number and is comprised between 3 and 100, preferably comprised between 7 and 14, more preferably equal to 7;

for POS1C compounds:

A, B, D, E, R, RF and d are defined as above,

R^{III} is an alkyl group or an atom of hydrogen,

h is a whole number comprised between 1 and 40, preferably between 2 and 10;

r_1, r_2, r_3, x_1, x_2, x_3, in each repetition of the oligomer o, are selected independently between 0 and 1, assuming that:

– r_1, r_2 and r_3 are not simultaneously 0,

– x_1, x_2, x_3 are not simultaneously 0, and

– in at least two repetitions of the oligomer o, x_1 is 1;

– in at least one repetition of the oligomer o, r_1 is 1

for POS2A compounds:

p, R, RF, A, B, D, E, u, v, z and d are defined as above;

W is a linear C2-C3 alkenyl group, vinyl or allyl;

for POS2B compounds:

r_1, r_2, r_3, x_1, x_2, x_3, o, h, W, R, RF, A, B, E, D and d are defined as above.

2. The compound according to claim 1, having the formula POS1A and a viscosity comprised between 100 and 300 cP, preferably comprised between 150 cP and 250 cP.

3. The compound according to claim 1, having the formula POS1B and a viscosity comprised between 80 cP and 180 cP.

4. The compound according to claim 1, having the formula POS1C and a viscosity comprised between 10 cP and 40 cP.

5. The compound according to claim 1, having the formula POS2A and a viscosity comprised between 100 cP and 300 cP.

6. The compound according to claim 1, having the formula POS2B and a viscosity comprised between 10 cP and 50 cP.

7. A composition, particularly for preparing supports for temporary adhesion of adhesive films, comprising:

– at least one compound selected among compounds POS1A, POS1B and POS1C as defined in claim 1,

– at least one compound selected among compounds POS2A and POSB as defined in claim 1, and

– at least one hydrosilylation catalyst.

8. The composition according to claim 7, wherein said at least one catalyst is selected among physical catalysts, preferably ultraviolet light, and chemical catalysts such as organic peroxides and complexes of transition metals.

9. The composition according to claim 8, wherein said organic peroxide is selected among t-butyl peroxide, AIBN, benzoyl peroxide, and mixtures thereof.

10. The composition according to claim 8, wherein the complex of transition metals is selected among complexes of platinum, complexes of palladium, salts of lead, salts of tin and mixtures thereof.

11. The composition according to claim 10, wherein the platinum complex is chloroplatinic acid.

12. The composition according to claim 11, wherein the chloroplatinic acid is further complexed with one or more vinylsiloxanes, preferably divinyltetramethyldisiloxane.

13. The composition according to claim 10, wherein the hydrosilylation catalyst is a complex of platinum and is used in a quantity comprised between 0.01 and 1 parts by weight per 100 parts of mixture (POS1 + POS2).

14. The composition according to claim 10, wherein the hydrosilylation catalyst is chloroplatinic acid complexed with one or more vinylsiloxanes and is used in a quantity comprised between 1 and 500 parts by weight of platinum per million of parts by weight of combined mixture (POS1 + POS2).

15. The composition according to claim 7, further comprising at least one of the following ingredients:

– dialkyl maleates, preferably bis(dimethoxyethyl)maleate, and

– dialkyl fumarates.

16. A crosslinked composition obtainable by applying heat to a composition according to claim 7.

17. The composition according to claim 16, in the form of a film.

18. A laminated element, particularly as a support for temporary adhesion of adhesive films, comprising:

– a crosslinked film according to claim 17, and

– a polymeric foundation material.

19. The laminated element according to claim 18, wherein the polymeric foundation material is selected from the group consisting of polyethylene terephthalate, polytetramethylene terephthalate, polyethylene 2,6–naphthalate, polyethylene–1,4–cyclohexylene, dimethylene terephthalate, polyethylene terephthalate/adipate, polyethylene terephthalate/sebacate, polypropylene, PVC, polyethylene and mixtures thereof.

20. A method for preparing the POS1A compounds as defined according to claim 1, comprising the step of reacting a compound having the formula (I–1A):

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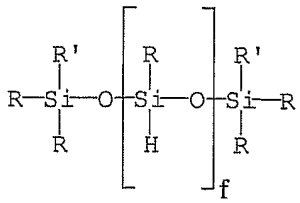


where

f is (f_1+f_2) and preferably is a whole number comprised between 3 and 200, more preferably comprised between 30 and 40;

R and R' are defined as in the preceding claims;

with at least one fluorinated compound selected from the group consisting of:

1) fluorinated terminal olefins, optionally comprising a heteroatom inside the chain, said heteroatom being selected among oxygen, nitrogen and sulfur;

and

2) fluorinated primary alcohols, optionally comprising a heteroatom inside the chain, said heteroatom being selected among oxygen, nitrogen or sulfur.

21. The method according to claim 20, wherein the olefins are selected from the group consisting of:

i) $C_nF_{2n+1}CH=CH_2$,

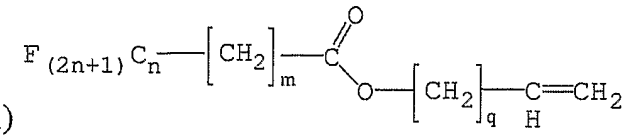
ii) $C_nF_{2n+1}CH_2CH=CH_2$,

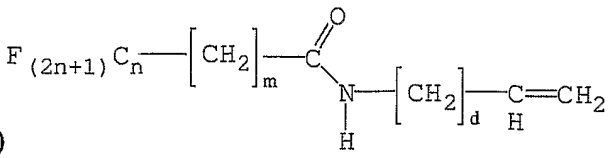
iii) $C_nF_{2n+1}(CH_2)_2O(CH_2)_q\ CH=CH_2$,

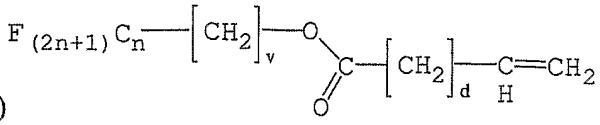
iv) $C_nF_{2n+1}(CH_2)_2OCH_2C_6H_4\ CH=CH_2$,

v) $C_nF_{2n+1}(CH_2)_2S(CH_2)_q\ CH=CH_2$,

vi) $C_nF_{2n+1}CH_2\ CH(OCH_3)CH_2O(CH_2)q\ CH=CH_2$,

vii) 

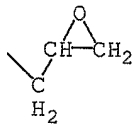
viii) 

ix) 

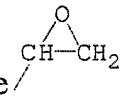
where n, m, v, q and d are defined as in the preceding claims.

22. The method according to claim 20, wherein the alcohols are selected from the group consisting of alcohols having the formula $C_nF_{2n+1}(CH_2)_l$–OH, where n is defined as in the preceding claims and l is a whole number comprised between 2 and 10.

23. The method according to claim 20, wherein the compound having the formula (I–1A) and the fluorinated compound further receive the addition of at least one epoxy compound selected among terminal olefins, optionally comprising a heteroatom inside the chain, selected among oxygen, nitrogen and sulfur, and further comprising an epoxy terminal group D selected between:

– ethylene oxide, 

and

– propylene oxide 

24. The method according to claim 23, where the epoxy olefins are selected from the group consisting of:

i) D–$(CH_2)_g$–CH=CH_2,

ii) D–$(CH_2)_d$ –O–$(CH_2)_g$–CH=CH_2,

iii) D–$(CH_2)_d$ –S–$(CH_2)_g$–CH=CH_2,

where D is the epoxy group, g is a whole number comprised between 1 and 20, and d is defined as above.

25. The method according to claim 23, where for one mole of

compound having the formula (I–1A), the fluorinated compound is present in a quantity comprised between 1 and 100 moles, preferably between 5 and 20 moles, and for 1 mole of fluorinated compound the epoxy compound is present in a quantity comprised between 0 and 0.5 moles.

26. The method according to claim 20, wherein the compound having the formula (I–1A) is selected among:

i) polymethyl hydrosiloxanes,

ii) polyethyl hydrosiloxanes,

iii) copolymers of (methyl-hydro)-(dimethyl hydrosiloxanes), and

iv) mixtures thereof.

27. The method according to claim 20, wherein the fluorinated compound is selected among the olefins having the formula 1), the reaction is performed in atmosphere of nitrogen, at a temperature comprised between 100°C and 150°C and:

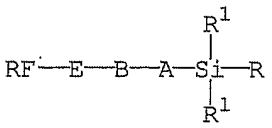
– if the olefins boil above approximately 60°C, in the presence of a catalyst selected among one or more organic peroxides;

– if the olefins boil below approximately 60°C, in the presence of a catalyst selected among one or more platinum-based catalysts.

28. The method according to claim 20, wherein the fluorinated compound is selected among fluorinated alcohols having the formula 2) and the reaction is performed under a constant stream of nitrogen in the presence of a catalyst selected among catalysts based on tin, cobalt, copper, zinc, and mixtures thereof.

29. A method for preparing the POS1B compounds as defined according to claim 1, comprising the steps of:

i) synthesizing a fluorinated base monomer having the formula (a–1B)



where A, B, E, R and RF are defined as in the preceding claims, and R^1 is selected between chlorine and –OR;

and where:

a) if B is oxygen or –NH–, step i) comprises putting in contact:

– at least one silicone unit having the general formula

$$H–SiR^1_{(3-d)}\,R_d$$

where d is 1,

– with at least one compound selected among:

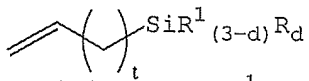
1) fluorinated terminal olefins, preferably one of the olefins i)–ix) according to claim 21;

and, if R^1 is –OR,

2) fluorinated primary alcohols, preferably one of the alcohols according to claim 22;

b) if B is sulfur, step i) comprises:

b1) putting in contact a silicone unit having the formula

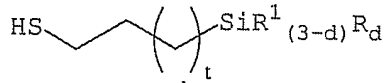


where t is 0 or 1 and d, R and R^1 are defined as in the preceding claims,

with one or more primary fluorinated thiols, preferably thiols having the formula $C_nF_{2n+1}(CH_2)_l–SH$, where n and l are defined as in the preceding claims;

or

b2) putting in contact a silicone unit having the formula

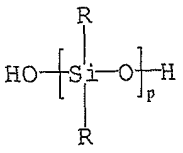


where d is 1, t, R and R^1 are defined as in the preceding claims,

with at least one terminal fluorinated olefin, preferably one of the olefins i)–ix) according to claim 21;

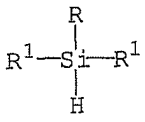
ii) mixing the fluorinated monomer (a–1B) synthesized in step i)

with:



– at least one silicone unit (b–1B)

and



– at least one silicone unit (c–1B)

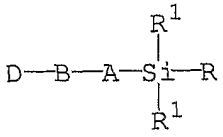
where p, R and R^1 are defined as in the preceding claims;

iii) polymerizing the product of the preceding step;

iv) ending the polymerization at the chosen degree of viscosity, by adding to the product of the preceding step a silicone unit (e–1B) having the formula R^1–$SiR_dH_{(3-d)}$ where d is comprised between 0 and 3, R and R^1 are defined as in the preceding claims.

30. The method according to claim 29, wherein step i) occurs in a solvent selected among toluene, alkanes, ethers, and mixtures thereof, in an atmosphere of nitrogen, in the presence of at least one catalyst preferably selected among organic peroxides and azonitrile compounds, at a temperature comprised between 60°C and 130°C.

31. The method according to claim 29, wherein in step ii) a monomer (d–1B) is also added having the formula



where A, B, D, R and R^1 are defined as in the preceding claims.

32. The method according to claim 31, wherein in step ii), for 1 mole of silicone unit (b–1B), the fluorinated monomer (a–1B) is present in a quantity comprised between 0.25 and 0.75 moles, the silicone unit (c–1B) is present in a quantity comprised between 0.25 and 0.75 moles, the silicone unit (d–1B) is present in a quantity comprised between 0 and 0.5 moles and the silicone unit (e–1B) is present in a quantity comprised between 0.005

and 0.2 moles.

33. The method according to claim 29, where if R^1 is chlorine, step iii) is preceded by a further step of washing the product of step ii) with water.

34. The method according to claims 29 and 33, wherein step iii) comprises bringing the product of step ii) to a temperature comprised between 130°C-150°C in the presence of an agent selected among:

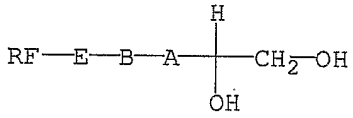
– at least one strong acid, preferably trifluoroacetic acid, or

– at least one base, preferably barium or strontium hydroxide.

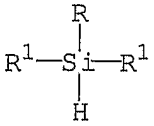
35. The method according to claim 29, wherein in step iii) the monomer (d–1B) is also added in a quantity comprised between 0.002 and 0.1 moles per mole of unit (b–1B).

36. A method for preparing the POS1C compounds as defined according to claim 1, comprising the steps of:

i) reacting a fluorinated glycol (a–1C) having the formula



where the variables are defined as in the preceding claims, with at least one silicone unit (c–1C) having the formula



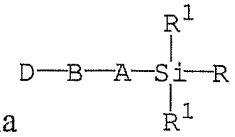
where R^1 is chlorine and R is defined as in the preceding claims,

ii) washing the product of step i) with water, and ending the polymerization at the chosen degree of viscosity by adding to the product of step i) a silicone unit (e–1C) having the formula:

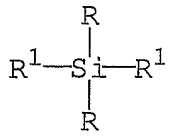
$$R^1\text{–}SiR_dH_{(3-d)}$$

where R^1 is chlorine and d is comprised between 0 and 3 and R is defined as in the preceding claims.

37. The method according to claim 36, wherein in step i) one also adds at least one monomer selected among:



– monomers (d–1C) having the formula



– monomers (b–1C) having the formula

where R^1 is chlorine and A, B, D and R are defined as in the preceding claims.

38. The method according to claim 36, wherein the fluorinated glycol (a–1C) is used in mixture with one or more non-fluorinated glycols selected among monomer (b–1B) as defined in claim 25, propylene glycol, ethylene glycol and hexanediol, said non-fluorinated glycols being present in a total quantity comprised between 0 and 0.5 moles per mole of fluorinated glycol (a–1C).

39. The method according to claim 37, wherein for 1 mole of fluorinated glycol (a–1C), the unit (b–1C) is present in a quantity comprised between 0 and 0.5 moles, the unit (c–1C) is present in a quantity comprised between 0.25 and 1 moles, the unit (d–1C) is present in a quantity comprised between 0 and 0.5 moles, and the unit (e–1C) is present in a quantity comprised between 0.005 and 0.2 moles.

40. The method according to claim 36, wherein step i) is performed under a stream of nitrogen, at a temperature comprised between 30°C and 60°C, in a solvent selected among toluene, acetonitrile, t-butyl methyl ether and mixtures thereof.

41. A method for preparing the POS2A compounds as defined according to claim 1, wherein said method comprises the steps of:

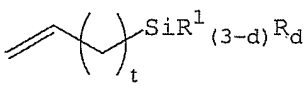
a) if the fluorinated portion RF is inserted before the preparation of the skeleton of the compound,

a–i) preparing a fluorinated silicone unit (a–2A) identical to the silicone unit (a–1B) according to step i) of claim 29;

a–ii) mixing:

– the silicone unit (a–2A) obtained from step a–i), with

– at least one silicone unit (c–2A) having the formula



where the variables are defined as in the preceding claims, and with

– at least one silicone unit (b–2A) identical to the unit (b–1B) as defined in claim 29;

a–iii) polymerizing the product of step ii);

a–iv) adding to the product of step iii) at least one silicone unit selected from the group consisting of:

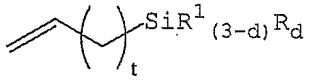
– silicone unit (e–2A) having the formula R^1-$SiR_dW_{(3-d)}$,

where d is comprised between 0 and 3 and the other variables are defined as in the preceding claims;

alternatively

b) if the fluorinated portion RF is inserted after the preparation of the skeleton of the compound,

b–i) mixing:

– a silicone unit (c–2A) having the formula  with

– a silicone unit (b–2A) identical to the unit (b-1B) as defined in claim 29, and with

– at least one silicone unit (e–2A);

where the variables are defined as in the preceding claims, it being understood in any case that the unit (c–2A) is quantitatively in excess with respect to the other units;

b–ii) adding to the product of step b–i) at least one iodofluorinated unit having the general formula $C_nF_{2n+1}X$, where X can be –Cl, –Br or, preferably, –I, where the moles of

iodofluorinated unit are less than the moles of the W-group containing units;

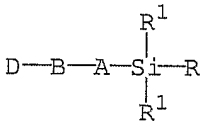
b–iii) eliminate the X group from the product of step b–ii) where:

b–iii–1) if an unsaturated derivative is to be obtained, step b–iii) comprises treating the product of step b–ii) with a strong base,

or

b–iii–2) if a saturated derivative is to be obtained, step b–iii) comprises treating the product of step b–ii) with a mixture comprising at least one radical initiator and at least one organic derivative of tin.

42. The method according to claim 41, options a) and b), wherein in step a–i) or b–i) one also adds a monomer (d–2A) having the formula:



where A, B, D, R and R^1 are defined as in the preceding claims.

43. The method according to claim 42, option a), wherein for 1 mole of silicone unit (b–2A), the fluorinated monomer (a–2A) is present in a quantity comprised between 0.25 and 0.75 moles, the unit (c–2A) is present in a quantity comprised between 0.25 and 0.75 moles, the unit (d–2A) is present in a quantity comprised between 0 and 0.5 moles, and the unit (e–2A) is present in a total quantity comprised between 0.005 and 0.2 moles.

44. The method according to claim 42, option b), wherein for 1 mole of silicone unit (b–2A), the unit (c–2A) is present in a quantity comprised between 0.5 and 1 moles, the unit (d–2A) is present in a quantity comprised between 0 and 0.5 moles, and the silicone unit (e–2A) is present in a total quantity comprised between 0.05 and 0.15 moles.

45. The method according to claim 41 option a), wherein step a–i) is performed in a stream of nitrogen and:

– if R^1 is chlorine, in a solvent selected among toluene, hexane, heptane and mixtures thereof, at a temperature comprised between 30° and 80°C,

or

– if R^1 is alkoxy, in a solvent selected among toluene, hexane, heptane and mixtures thereof, at a temperature comprised between 60°-130°C.

46. The method according to claim 41 option b), wherein step b–i) is performed under a stream of nitrogen, in a solvent selected among toluene, hexane, heptane and mixtures thereof, at a temperature comprised between 30° and 60°C.

47. The method according to claim 41 options a) and b), wherein if R^1 is chlorine, steps a–iii) and b–ii) are preceded by a further step of washing the product respectively of steps a–ii) and b–i) with water.

48. The method according to claims 41 option a) and 47, wherein the step a–iii) comprises bringing the product of step a–ii) to a temperature comprised between 130°C-150°C in the presence of an agent selected among:

– at least one strong acid, preferably trifluoroacetic acid, or

– at least one base, preferably barium or strontium hydroxide.

49. The method according to claim 41 option b), wherein step b–ii) is performed in an atmosphere of nitrogen, at a temperature comprised between 80° and 120°C, in the presence of a radical initiator, preferably AIBN, and of at least one reducing compound, preferably sodium metabisulfite, even more preferably sodium metabisulfite in a 20-30% aqueous solution.

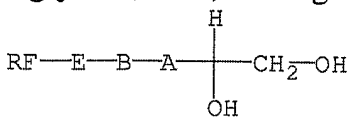
50. The method according to claim 41 option b), wherein in step b–iii–1) the strong base is a hydroxide of an alkaline metal, preferably sodium hydroxide, even more preferably sodium hydroxide in a 25-30% water-alcohol solution.

51. The method according to claim 41 option b), wherein in step b–

iii–2) the fluorinated polymer is treated with a combination of a radical initiator, preferably AIBN, and of an organic compound of tin, preferably butyl tin hydride, at a temperature comprised between 60° and 100°C, preferably equal to 80°C.

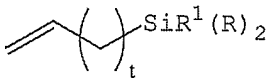
52. A method for preparing the POS2B compounds as defined according to claim 1, comprising the steps of:

i) reacting a fluorinated glycol (a–2B) having the general formula:



where the variables are defined as in the preceding claims,

with at least one silicone unit (c–2B) having the formula



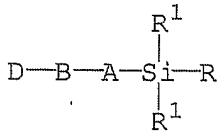
where R^1 is chlorine and the other variables are d efined as in the preceding claims;

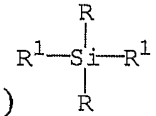
ii) washing the product of step i) with water, and ending the polymerization at the chosen degree of viscosity by adding to the product of the preceding step at least one silicone unit selected from the group consisting of:

– silicone unit (e–2B) having the formula $R^1\text{-}SiR_dW_{(3-d)}$,

where R^1 is chlorine, d is an integer comprised between 0 and 3 and the other variables are defined as in the preceding claims.

53. The method according to claim 52, wherein in step i) one also adds at least one monomer selected among:

– monomer (d–2B) 

– monomer (b–2B) 

where R^1 is chlorine and A, B, D, R are defined as in the preceding claims.

54. The method according to claim 53, wherein for 1 mole of fluorinated glycol (a–2B), the unit (b–2B) is present in a quantity comprised between 0 and 0.5 moles, the unit (c–2B) is present in a quantity comprised between 0.25 and 1 moles, the unit (d–2B) is present in a quantity comprised between 0 and 0.5 moles, and the unit (e–2B) is present in a total quantity comprised between 0.005 and 0.2 moles.

55. The method according to claim 52, wherein step i) is performed in a stream of nitrogen, at a temperature comprised between 30° and 60°C and in a solvent selected among toluene, acetonitrile, t-butyl methyl ether, and mixtures thereof.

56. The method according to claim 52, wherein step ii) is preceded by a further step of washing the product of step i) with water.

57. The method according to claim 52, wherein the fluorinated glycol (a–2B) is used in mixture with:

– silicone unit (b–1B) as defined in claim 26,

and/or with

– one or more non-fluorinated glycols selected among propylene glycol, ethylene glycol and hexanediol,

where the non -fluorinated monomers are present in a total quantity comprised between 0 and 0.5 moles for 1 mole of fluorinated glycol (a–2B).

58. A method for preparing a laminated element as defined in claim 18, comprising the steps of:

a) mixing one or more POS2 compounds as defined in claim 1 with at least one catalyst of the hydrosilylation reaction preferably as defined in claims 7 to 14, and optionally with one or more ingredients selected from the group consisting of:

– dialkyl maleate, preferably bis(dimethoxyethyl)maleate, and dialkyl fumarates;

b) adding one or more POS1 compounds as defined in claim 1 to the product of step a),

c) applying the product of step b) in one or more layers to a polymeric foundation material as defined in claim 19, wherein for each layer the product of step b) is applied in a quantity comprised between 0.1 and 3 g/m^2, preferably between 0.3 and 1.2 g/m^2;

d) applying heat to the product of step c) for a time comprised between 10 seconds and 5 minutes.

59. The method according to claim 58, wherein step c) is provided with the aid of a solvent selected among toluene, t-butyl methyl ether, C4–C8 alkane, and mixtures thereof.

60. The method according to claim 58, wherein a further mixing step is performed between steps a) and b) and/or after step b).

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/006625

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G77/24 C08G77/20 C08G77/14 C08G77/12 C08G77/385
C08L83/08 C08L83/06 C09D183/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G C08L C09D

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 472 215 A (DOW CORNING TORAY SILICONE COMPANY, LIMITED) 26 February 1992 (1992-02-26) example 1 Invention Example 4 claims 1-5	1,2,5,7, 8,10,11, 16
Y		18-35, 41-51, 58-60
X	US 2002/061969 A1 (SHIONO MIKIO ET AL) 23 May 2002 (2002-05-23) page 12, first formula	1
X	GB 2 096 631 A (GEC US) 20 October 1982 (1982-10-20) claims 1,5,11	1
A		1,20,41

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 October 2005	21/10/2005

Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 567 970 A (DOW CORNING TORAY SILICONE COMPANY, LIMITED) 3 November 1993 (1993-11-03) claim 7; examples 2,4	1
Y		18,19, 58-60
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A	EP 0 621 316 A (SHIN-ETSU CHEMICAL CO., LTD) 26 October 1994 (1994-10-26) page 2, lines 35-40 page 3, lines 14-40 page 8, line 40 page 14, line 30; claim 4	1-3,5, 7-35, 41-51, 58-60

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