



- wherein a is 0 or 1, or 2,
- wherein c is 0 or 1, or 2,
- wherein a + c = 0 or 1 or 2,  
wherein R<sup>1</sup> represents a C<sub>1</sub> to C<sub>13</sub>  
saturated or unsaturated, substituted or  
unsubstituted, aliphatic, cycloalkane or  
aromatic monovalent hydrocarbon radical.
- wherein R<sup>2</sup> represents an aliphatic organic  
radical containing 1 to 8 carbon atoms,  
selected in particular from the alkyl  
radicals, alkylether radicals, alkylester  
radicals, alkylketone radicals, alkylcyano  
radicals, or an aralkyl radical containing 7  
to 13 carbon atoms, and wherein if relevant  
more than one alkoxy group in the silane of  
formula (1) for R<sup>2</sup>, may differ in the  
alkoxy groups, and
- wherein R<sup>4</sup> represents a substituted or  
unsubstituted, saturated or unsaturated, C<sub>1</sub>  
to C<sub>13</sub> aliphatic, cycloalkane or aromatic  
monovalent hydrocarbon radical, and wherein  
R<sup>4</sup> may optionally be identical to R<sup>1</sup>.

16. The product obtained according to one of claims 14 to 15 for the preparation of single-component polysiloxane compositions which are stable on storage in the absence of moisture and which crosslink to form an elastomer in the presence of moisture.

PATENTS ACT 1952

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Complete Specification for the Invention entitled:

"PROCESS FOR THE PREPARATION OF DIORGANOPOLYSILOXANES  
HAVING ALKOXY END GROUPS"

The following statement is a full description of this invention,  
including the best method of performing it known to us:-

PROCESS FOR THE PREPARATION OF DIORGANOPOLYSILOXANES  
HAVING ALKOXY END GROUPS

The present invention relates to a process for the preparation of diorganopolysiloxanes having alkoxy end groups, termed PF (polymers containing functional groups) below, and to the use, of at least some of these, in particular as one of the essential constituents in single-component organopolysiloxane elastomer compositions which are stable on storage and in the absence of moisture and which crosslink under atmospheric humidity at ambient temperature, which are termed compositions for cold-vulcanisable elastomer (CVE) compositions below.

It is known to prepare these PFs by reacting a dialkoxysilane, a trialkoxysilane or a tetraalkoxysilane with a diorganopolysiloxane oil comprising a hydroxyl group linked to the silicon atom at each end of its chain, but it is necessary to use a catalyst. Numerous patents have been filed claiming the use of catalysts specifically for this reaction for the introduction of functional groups.

US Patent 3,542,901 proposes an amine as the catalyst. This catalyst is effective but the reaction is fairly slow (for example 15 to 30 min at 60°C for fairly reactive alkoxy silanes such as  $\text{Si}(\text{OCH}_3)_4$  or  $\text{Vi Si}(\text{OCH}_3)_3$ ). With alkoxy silanes of low reactivity, it is necessary to make use of very much longer times, or to obtain only incomplete reactions. Now, it is known that

the presence of residual silanols is generally adverse for the stability (see US 4,489,191-A and also French Patent Application Nos. 2,597,876 and 2,597,877).

Moreover, it is difficult to remove the amine

5 completely, which may have an adverse effect on the stability of the composition on storage; it may also cause the appearance of yellowish discolorations, either during storage of the mastic or on the crosslinked product.

10 It is for this reason that numerous other catalytic systems have been proposed. The following may be mentioned:

- potassium acetate : US 3,504,051
- diverse inorganic oxides : FR 1,495,011
- 15 - organic titanium derivatives : US-A-4,111,890
- titanate plus amine : US 3,647,846
- alkoxyaluminium chelate : GB-A-2,144,758
- N,N'-disubstituted hydroxylamine : FR-A-20 2,508,467
- carboxylic acid plus amine : FR 2,604,713
- carbamates : EP 0,210,402
- organic compounds containing an oxime group : FR 2,597,875.

25 Some of these catalysts are slightly more active than the amines, but it is nevertheless necessary to heat to 60-70°C in order to obtain times of 5 to 10 minutes for introduction of the functional

groups. Moreover, these catalysts, or their residues, may have an adverse influence on the stability on storage; in particular in the presence of setting catalysts, as well as on the properties of the crosslinked products because it is difficult or impossible to remove them completely after reaction.

Patent Application FR 88.15312, filed on 4 November 1988 in the name of the Applicant, also describes a process for the preparation of diorganopolysiloxanes having alkoxy end groups using lithium oxide as the catalyst for the introduction of functional groups.

Another process for making oils containing functional groups (PF) consists in using mixed silanes having, in addition to the alkoxy groups, a water-soluble group such as an amido, amino, carbamate or oxime group, etc., if appropriate in the presence of a known catalyst for the introduction of functional groups and a polyalkoxysilane.

Processes of this type are described, in particular, in Patents US-A-3,697,568, US-A-3,896,079 and EP-A-69,256.

These processes are effective but necessitate the use of costly mixed silanes. Moreover, the organic products resulting from the water-soluble groups after reaction may have an adverse effect on the CVE composition (see pages 4 and 5 of French Patent FR-A-2,543,562 on this subject).

The aim of the present invention is to propose catalysts for the introduction of functional groups which are very effective for obtaining straight-chain diorganopolysiloxanes comprising at least one alkoxy group linked to a silicon atom at each end of their chain (polymers termed PF below or oils containing functional groups).

Another aim of the present invention is to propose catalysts for introducing functional groups which enable PF to be obtained by carrying out the reaction at ambient temperature, in particular using  $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ ,  $\text{CH}_2=\text{CH}-\text{Si}(\text{OCH}_3)_3$  or  $\text{MeViSi}(\text{OCH}_3)_2$  as the agent for introducing functional groups (Me representing the methyl group  $-\text{CH}_3$  and Vi representing the vinyl group  $-\text{CH}=\text{CH}_2$ ).

Another aim of the present invention is to propose catalysts for introducing functional groups which enable PF to be obtained, at ambient temperature, in a time of less than 15 minutes, advantageously of less than 10 minutes and preferably of 5 minutes or less, in particular using one of the abovementioned crosslinking agents as the crosslinking agent.

Another aim of the present invention is the use of inexpensive catalysts which are available commercially (in the chemical sector) and may be used, even in a large quantity, during the reaction for the introduction of functional groups.

Another aim of the present invention is to

propose catalysts for introducing functional groups which may easily be neutralised at the end of the reaction for the introduction of functional groups, in particular by a silyl phosphate.

5                    Another aim of the present invention is to propose catalysts for introducing functional groups which may be neutralised at the end of the reaction for the introduction of functional groups without there being any need for urgency in carrying out this neutralisation, that is to say it is possible to start the neutralisation, for example, one hour after the reaction for the introduction of functional groups has been completed.

15                    Another aim of the present invention is a catalyst for introducing functional groups which, after its neutralisation and, if appropriate, the devolatilisation of the reaction mass at the end of the reaction for the introduction of functional groups, allows the preparation, using the PF obtained  
20 (containing the reaction product resulting from neutralisation of the catalyst), of compositions for cold-vulcanisable elastomers (CVE) which are stable on storage in the absence of moisture and which crosslink under atmospheric humidity at ambient temperature.

25                    Such compositions have the advantage of not necessitating the use of compounds (scavengers) intended to remove the final traces of silanols, such as those described in Patent Nos. EP 69,256,



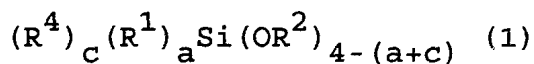
EP 104,179 and FR 2,543,562.

A process for the preparation of linear diorganopolysiloxane containing at least one alkoxy group bound to a silicon atom at each end of its chain,

5 comprising the step of reacting the following compounds

- 100 parts, by weight, of at least one linear diorganopolysiloxane containing an hydroxy group bound to a silicon atom at each end of its chain,

- 0.35 to 6 parts, by weight, of at least one polyalkoxysilane of formula:



- 0.5 to 15 parts, by weight, of at least one alcohol, preferably methanol, in the presence of a catalytically effective amount of sodium hydroxide  
15 or potassium hydroxide,

- wherein a is 0 or 1, or 2,

- wherein c is 0 or 1, or 2,

- wherein a + c = 0 or 1 or 2,

wherein R<sup>1</sup> represents a C<sub>1</sub> to C<sub>13</sub>

20 saturated or unsaturated, substituted or unsubstituted, aliphatic, cycloalkane or aromatic monovalent hydrocarbon radical.



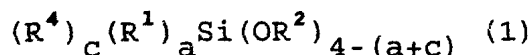
5                   -       wherein  $R^2$  represents an aliphatic organic radical containing 1 to 8 carbon atoms, selected in particular from the alkyl radicals, alkylether radicals, alkylester radicals, alkylketone radicals, alkylcyano radicals, or an aralkyl radical containing 7 to 13 carbon atoms, and wherein if relevant more than one alkoxy group in the silane of formula (1) for  $R^2$ , may differ in the alkoxy groups, and

10                   -       wherein  $R^4$  represents a substituted or unsubstituted, saturated or unsaturated,  $C_1$  to  $C_{13}$  aliphatic, cycloalkane or aromatic monovalent hydrocarbon radical, and wherein

15                    $R^4$  may optionally be identical to  $R^1$ .

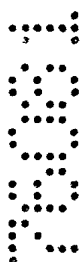
According to a variant of the invention, a process for the preparation of straight-chain diorganopolysiloxane comprising at least one alkoxy group linked to a silicon atom at each end of its chain has also been found, the said process being characterised in

20                   that one mole of at least one diorganopolysiloxane comprising a hydroxyl group linked to a silicon atom at each end of its chain is reacted with 2 to 6 moles of at least one polyalkoxysilane of formula:



25                   in the presence of a catalytically effective amount of sodium hydroxide or potassium hydroxide,

- where a is 0 or 1, or 2,



- where  $c$  is 0 or 1, or 2,
- where  $a + c = 0$  or 1 or 2,
- where  $R^1$  represents a substituted or unsubstituted, saturated or unsaturated,  $C_1$  to  $C_{13}$  aliphatic, cycloalkane or aromatic monovalent hydrocarbon radical,
- where  $R^2$  represents an aliphatic organic radical having from 1 to 8 carbon atoms, chosen, in particular, from alkyl radicals, alkyl ether radicals, alkyl ester radicals, alkyl ketone radicals, alkyl cyano radicals or an aralkyl radical having from 7 to 13 carbon atoms, it being understood that the alkoxy groups in the silane of formula (1) may each have a different meaning for  $R^2$  or the same meaning, and
- where  $R^4$  represents a substituted or unsubstituted, saturated or unsaturated,  $C_1$  to  $C_{13}$  aliphatic, cycloalkane or aromatic monovalent hydrocarbon radical, it being possible for  $R^4$  to be identical to  $R^1$ .

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These two variants exist because it has been found by the Applicant that during the introduction of functional groups into the polydiorganosiloxanes by the alkoxy silanes, using strong alkaline catalysis, degradation reactions of the polymers, containing functional groups, which are obtained take place. Following an in-depth kinetic study of these various

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reactions involved, it has been found that under certain conditions these adverse degradation reactions may be substantially slowed down.

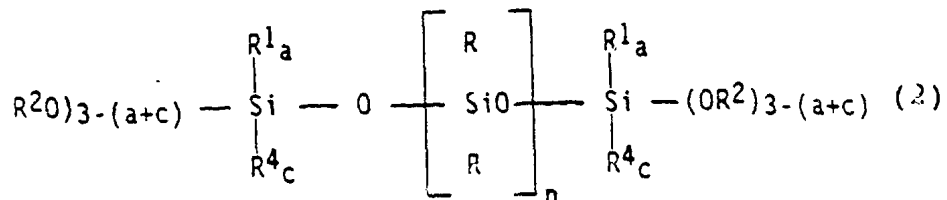
Thus, the stronger the base used as catalyst  
5 the more it is the quantity of polyalkoxysilanes introduced, in synergism with the catalyst, which is a predominant parameter in the degradation process of the polymers containing functional groups. It is for this reason that one mole of a diorganopolysiloxane  
10 comprising a hydroxyl group linked to a silicon atom at each end of its chain is reacted with 2 to 6 moles of at least one polyalkoxysilane of formula (1), knowing that only one of the alkoxy groups of a  
polyalkoxysilane reacts with a silanol group of a  
15 diorganopolysiloxane, which corresponds to one to three times the stoichiometric quantity.

An excess of polyalkoxysilanes increases the rate of the degradation reactions; an excess of polyalkoxysilanes is understood to be an amount of  
20 these polyalkoxysilanes which is 3 times higher than the stoichiometric quantity. However, the degradation reactions may be distinctly slowed down when at least one alcohol, such as methanol, ethanol and propanol, individually or as a mixture, is present in the  
25 reaction mixture and its quantity is between 0.5 and 15 parts by weight, preferably between 2 and 5 parts by weight, per 100 parts by weight of at least one polydiorganopolysiloxane.

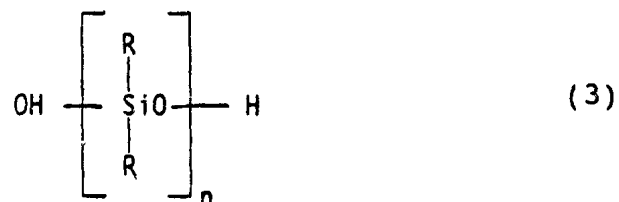
In practice, an alcohol is used which has a boiling point of below or equal to 100°C.

Another aim of the present invention is the use of straight-chain diorganopolysiloxanes, in particular those comprising at least two alkoxy groups at each end of the chain, obtained by the process of the present invention for the preparation of single-component polysiloxane compositions which are stable on storage in the absence of moisture and which crosslink to form an elastomer in the presence of moisture.

More precisely, the diorganosiloxanes comprising at least one alkoxy group at each end of their chain have the formula:



and the diorganopolysiloxane comprising a hydroxyl group at each end of its chain has the formula:



- where R<sup>1</sup>, R<sup>2</sup> and R<sup>4</sup> have the same meaning as that given above for the silane of formula (1),
- 20 - where the radicals R, which may be identical or

different, represent monovalent hydrocarbon radicals having from 1 to 10 carbon atoms, which may be substituted by halogen atoms or cyano groups; preferably, the radicals R are chosen from methyl, phenyl, vinyl and 3,3,3-trifluoropropyl radicals,

- 5 - where a is 0, or 1, or 2,
- where c = 0, or 1, or 2,
- where a + c = 0, or 1, or 2, and
- 10 - where n has a value sufficient to confer on the polymers of formula (2) and (3) a viscosity of 25 to 1,000,000 mPa s at 25°C, it being understood that the polysiloxane of formula (2) may have an average formula in which the value of n is higher or lower than the value of n in the diorganopolysiloxane (3) reacting with the silane of formula (1).

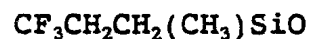
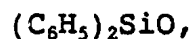
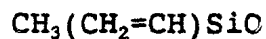
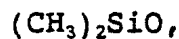
The radicals R mentioned above comprise:

- alkyl and halogenoalkyl radicals having from 1 to 10 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, 2-ethyl hexyl, octyl, decyl, 3,3,3-trifluoropropyl, 4,4,4-trifluorobutyl or 4,4,4,3,3-pentafluorobutyl radicals,
- 20 - cycloalkyl and halogenocycloalkyl radicals having from 1 to 10 carbon atoms, such as cyclopentyl, cyclohexyl, methylcyclohexyl, propylcyclohexyl, 2,3-difluorocyclobutyl or 3,4-difluoro-5-

methylcycloheptyl radicals,

- alkenyl radicals having from 2 to 4 carbon atoms, such as vinyl, allyl or but-2-enyl radicals,
- monocyclic aryl and halogenoaryl radicals having from 6 to 10 carbon atoms, such as phenyl, tolyl, xylyl, chlorophenyl, dichlorophenyl or trichlorophenyl radicals, and
- cyanoalkyl radicals in which the alkyl chains have from 2 to 3 carbon atoms, such as  $\beta$ -cyanoethyl and  $\beta$ -cyanopropyl radicals.

The following may be mentioned as specific examples of  $R_2SiO$  units present in the alpha,omega-dihydroxydiorganopolysiloxane of formula (3):



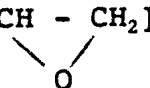
It must be understood that in the process according to the present invention a mixture consisting of alpha,omega-di(hydroxy)diorganopolysiloxane polymers which differ from one another in respect of the molecular weight and/or the nature of the groups linked to the silicon atoms may be used as polymer of formula (3). It must also be mentioned that the polymer of

formula (3) may optionally comprise monoorganosiloxy  $\text{RSiO}_{1.5}$  and/or  $\text{SiO}_2$  units, in a proportion of at most 2% relative to the number of diorganosiloxy units  $\text{R}_2\text{SiO}$ .

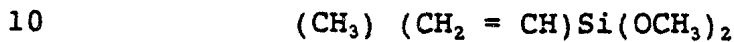
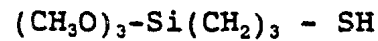
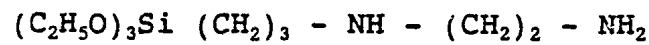
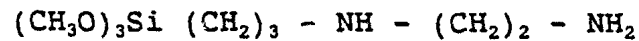
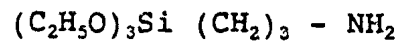
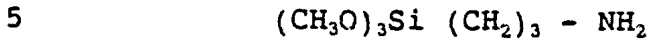
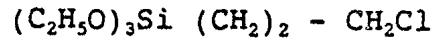
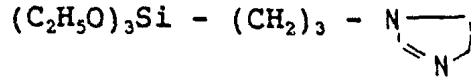
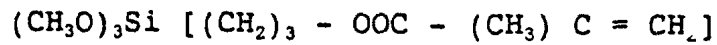
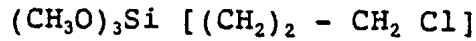
5 These alpha,omega-di(hydroxy)diorganopolysiloxane polymers are available commercially; in addition, they may be produced easily in accordance with techniques which are now well known.

Amongst the polyalkoxysilanes of formula  $(\text{R}^4)_c(\text{R}^1)_a\text{Si}(\text{OR}^2)_{4-(a+c)}$  which may be used in the process according to the present invention, those listed below may be mentioned in particular:

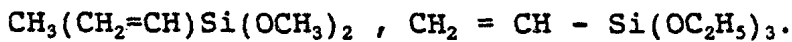
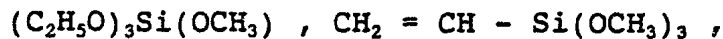
- 10
- 15
- 20
- 25
- $\text{Si}(\text{OCH}_3)_4$   
 $\text{Si}(\text{OCH}_2\text{CH}_3)_4$   
 $\text{Si}(\text{OCH}_2\text{CH}_2\text{CH}_3)_4$   
 $(\text{CH}_3\text{O})_3\text{SiCH}_3$   
 $(\text{C}_2\text{H}_5\text{O})_3\text{SiCH}_3$   
 $(\text{CH}_3\text{O})_3\text{SiCH} = \text{CH}_2$   
 $(\text{C}_2\text{H}_5\text{O})_3\text{SiCH} = \text{CH}_2$   
 $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{-CH} = \text{CH}_2$   
 $(\text{CH}_3\text{O})_3\text{Si} [\text{CH}_2\text{-(CH}_3\text{)C} = \text{CH}_2]$   
 $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{OCH}_3)$   
 $\text{Si}(\text{OCH}_2\text{-CH}_2\text{-OCH}_3)_4$   
 $\text{CH}_3\text{Si}(\text{OCH}_2\text{-CH}_2\text{-OCH}_3)_3$   
 $\text{CH}_2 = \text{CHSi}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$   
 $\text{C}_6\text{H}_5\text{Si}(\text{OCH}_3)_3$   
 $\text{C}_6\text{H}_5\text{Si}(\text{OCH}_2\text{-CH}_2\text{-OCH}_3)_3$   
 $(\text{CH}_3\text{O})_3\text{Si} [(\text{CH}_2)_3 - \text{O} - \text{CH}_2 - \text{CH} - \text{CH}_2]$







The most commonly used polyalkoxysilanes are:



15 With regard to the sodium hydroxide or potassium hydroxide used as the catalyst, both are widely available commercially; their formulae are, respectively, NaOH and KOH. When the reaction mixture does not contain alcohol, the sodium hydroxide or

20 potassium hydroxide is preferably used as a solution in an alcohol, such as methanol or ethanol; the amount of alcohol present is then negligible. In general, a quantity of alcohol of between 2 and 4 times the quantity by weight of sodium hydroxide or potassium

25 hydroxide is used.

A catalytically effective quantity of sodium hydroxide or potassium hydroxide is understood to be a

quantity such that the rate of reaction is appreciably increased, in particular using  $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ ,  $\text{CH}_2=\text{CH}-\text{Si}(\text{OCH}_3)_3$  or  $\text{MeViSi}(\text{OCH}_3)_3$ , as the agent for introducing functional groups. In the majority of cases, from 0.001 to 5 moles of sodium hydroxide or potassium hydroxide is used per 1 mole of silanol group  $=\text{SiOH}$  in the polydiorganopolysiloxane of formula (3), it being understood that in order to have 1 mole of  $=\text{SiOH}$ , 0.5 mole of polydiorganopolysiloxane of formula (3) is needed.

The temperature of the reaction according to the present invention is preferably between  $-10^\circ\text{C}$  and  $90^\circ\text{C}$  and more preferably between  $10^\circ\text{C}$  and  $50^\circ\text{C}$ .

The process according to the present invention is preferably carried out in the absence of moisture, for example in a closed reactor which is fitted with a stirrer and in which a vacuum has been produced and the air driven off has then been replaced by an anhydrous gas, for example nitrogen.

The reactants and the catalyst are charged into the reactor and when the reaction for the introduction of functional groups is complete the catalyst is neutralised and the reaction mass obtained is devolatilised in order to remove the alcohol formed during the reaction for the introduction of functional groups and the excess of agent for introducing functional groups (that is to say the silane of formula (1)).



Numerous products may be used to neutralise the catalyst for introducing functional groups (sodium hydroxide or potassium hydroxide), for example trichloroethyl phosphate or dimethylvinylsilyl acetate. However, it is preferred to use a silyl phosphate, such as, for example, those described in French Patent 2,410,004.

The devolatilisation is carried out, for example, under an absolute pressure of between 133 and 13332 pascals.

The patent application according to the present invention also relates to the use of diorganopolysiloxanes, in particular those comprising at least two alkoxy groups at each end of the chain, obtained by the process of the present invention, for the preparation of single-component polysiloxane compositions which are stable on storage in the absence of moisture and which crosslink to form an elastomer in the presence of moisture.

These compositions are obtained by adding (by weight):

- 0 to 250 parts of inorganic fillers,
- 0 to 20 parts, preferably 0 to 10 parts, of at least one additive chosen from aminoorganosilanes, aminoorganopolysiloxanes and guanidinoorganosilanes simultaneously carrying, per molecule:

- . (i) at least one C<sub>3</sub>-C<sub>15</sub> organic group linked by a SiC bond to the silicon atom and

substituted by at least one amino radical  
or one guanidino radical,

. (2i) and at least one C<sub>1</sub>-C<sub>3</sub> alkoxy radical  
or a C<sub>3</sub>-C<sub>6</sub> alkoxyalkyleneoxy radical, and

5 - an effective amount of condensation catalyst to  
100 parts of the polymer, containing functional groups,  
of formula (2) obtained by the process of the present  
invention (containing the product from the  
neutralisation of sodium hydroxide or potassium  
10 hydroxide).

An effective quantity of condensation  
catalyst is understood to be, for example, from 0.001  
to 1 part by weight of at least one compound of a metal  
generally chosen from tin, titanium and zirconium and  
15 their mixtures.

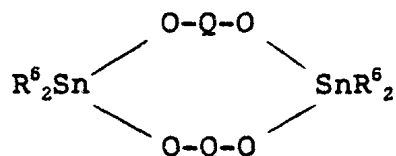
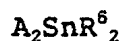
Condensation catalysts which may be used are  
tin monocarboxylates and dicarboxylates, such as tin 2-  
ethylhexanoate, dibutyltin dilaurate or dibutyltin  
diacetate (see the book by NOLL "Chemistry and  
20 technology of silicone", page 337, Academic Press, 1968  
- 2nd edition).

The hexacoordinated chelates of tin or  
valency IV, such as those described in European Patent  
Application EP-A-147,323 and the Patent US-A 4,517,337,  
25 which are cited as reference, are particularly  
appropriate.

Condensation catalysts which are also  
preferred are those which are a mixture of a

diorganotin bis( $\beta$ -diketonate) with an organic derivative of tin, also of valency IV, but free from any  $\beta$ -diketonato group and possessing at least one tin atom, each tin atom carrying two organic radicals bonded by a Sn-C bond, the other two valencies being satisfied by radicals chosen from organic or inorganic radicals bonded by a SnO or SnS bond, by halogen atoms, by hydroxyl groups and by oxygen atoms.

These organic derivatives of tin of valency IV which are free from any  $\beta$ -diketonato group may be, in particular, tin salts of the formulae:



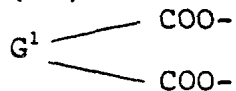
in which:

- $R^6$  represents a  $C_1$ - $C_{20}$  hydrocarbon radical, which may or may not be halogenated,
- A represents an organic or inorganic radical bonded to the tin atom by a Sn-O or Sn-S bond, or a halogen atom, and
- Q represents a  $C_2$ - $C_{10}$  alkylene radical.

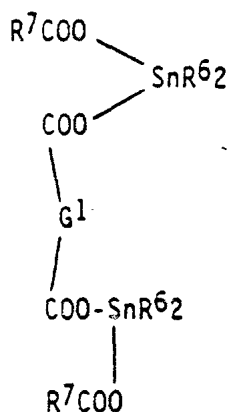
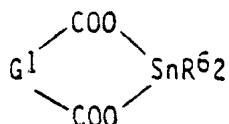
A may be chosen from the group comprising:

- (i) monocarboxylate radicals of formula  $R^7COO$ ,  $R^7$  being a  $C_1$ - $C_{20}$  hydrocarbon radical, which may or may not be halogenated,

. (2i) dicarboxylate radicals of formula



5 bonded to a single tin atom or to two tin atoms,  
leading to the two formulae:



in which  $\text{G}^1$  represents a divalent  $\text{C}_1\text{-C}_{15}$  hydrocarbon radical and  $\text{R}^7$  has the meaning given under (i), and

. (3i) dicarboxylate radicals of formula

10

$\text{R}^7\text{OCOG}^1\text{COO}$ , in which  $\text{R}^7$  and  $\text{G}^1$  have the meaning given, respectively, under (i) and (2i).

The above tin salts are well known and are described, in particular, in the NOLL publication  
15 mentioned above, the Patents US-A-3,186,963 and 3,862,919, Belgian Patent 842,305 and British Patent GB-A-1,289,900, which are cited as reference.

The inorganic fillers are used in an amount of from 0 to 250 parts, preferably from 5 to 200 parts, per 100 parts of PF of formula (2).

These fillers may be in the form of very  
5 finely divided products, the average particle diameter of which is less than 0.1 micrometre. These fillers include silicas produced by combustion and silicas produced by precipitation; their BET specific surface area is generally larger than 40 m<sup>2</sup>/g.

10 These fillers may also be in the form of more coarsely divided products having an average particle diameter of more than 0.1 micrometre. The following may be mentioned as examples of such fillers: ground  
15 quartz, diatomaceous silicas, calcium carbonate, calcine clay, titanium oxide of the rutile type, iron, zinc, chromium, zirconium and magnesium oxides, the various forms of alumina (hydrated or nonhydrated),  
boron nitride, lithopone, barium metaborate, barium  
20 sulphate and glass microspheres; their specific surface area is generally less than 30 m<sup>2</sup>/g.

These fillers may have been surface-modified by treatment with the various organosilicon compounds customarily used for this application. Thus, these organosilicon compounds may be organochlorosilanes,  
25 diorganocyclopolysiloxanes, hexaorganodisiloxanes, hexaorganodisilazanes or diorganocyclopolysiloxanes (French Patent FR-A-1,126,884, FR-A-1,136,885, FR-A-1,236,505; British Patent GB-A-1,024,234). In the

majority of cases, the treated fillers contain from 3 to 30% of their weight of organosilicon compounds.

The fillers may consist of a mixture of several types of fillers of different particle sizes; thus, for example, they may consist of 30 to 70% of finely divided silicas having a BET specific surface area of greater than 40 m<sup>2</sup>/g and 70 to 30% of more coarsely divided silicas having a specific surface area of less than 30 m<sup>2</sup>/g.

In order to improve, in particular, the adherence of the CVEs, the compositions according to the invention may optionally also contain from 0 to 20 parts, preferably from 1 to 15 parts, of at least one additive chosen from aminoorganosilanes, aminoorganopolysiloxanes and guanidineorganosilanes simultaneously carrying, per molecule:

- . (i) at least one C<sub>3</sub>-C<sub>15</sub> organic group bonded by a SiC bond to the silicon atom and substituted by at least one amino radical or one guanidino radical,
- . (2i) and at least one C<sub>1</sub>-C<sub>5</sub> alkoxy radical or one C<sub>3</sub>-C<sub>6</sub>alkoxyalkylene radical.

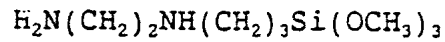
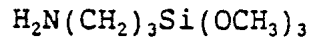
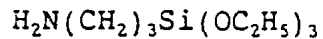
These additives and their modes of use are described, in particular, in the patents

US-A-2,574,311, US-A-2,832,754, US-A-2,930,809, US-A-2,971,864, US-A-3,341,563, US-A-3,686,375 and US-A-4,180,642.

Amongst these additives, the silanes of

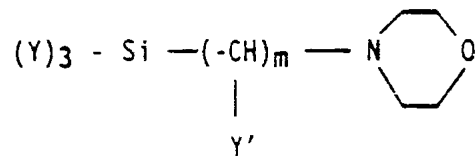


formula:



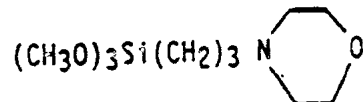
5 may be mentioned in particular.

Particularly suitable adherence promoters are the silanes of formula:

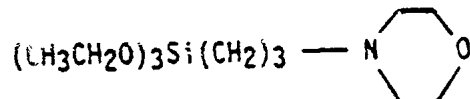


in which Y is an alkyl or alkoxy radical having from 1 to 4 carbon atoms inclusive, at least two of the radicals Y being alkoxy radicals, Y', which may be identical or different, are chosen from a hydrogen atom and an alkyl radical having from 1 to 3 carbon atoms inclusive and m is an integer between 3 and 10 inclusive.

15 Silanes which may be mentioned are:



gamma-morpholinopropyltrimethoxysilane



gamma-morpholinopropyltriethoxysilane.

These products and the process for their preparation are described by John L. SPEIER, J. Org. Chem., vol. 36, No. 21, 1971, page 3, 120.

In the text which follows and in the foregoing text, unless specifically indicated to the contrary, the percentages and the parts are by weight.

The following examples illustrate the invention, without restricting its scope.

In these examples:

$\bar{M}_n$  is the number-average molecular mass, and  $\eta$  is the viscosity expressed in mPa s.

EXAMPLE 1

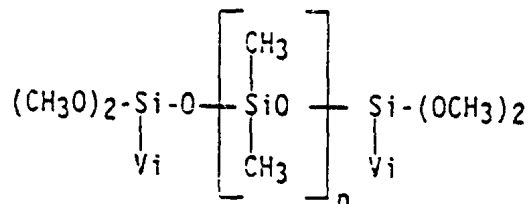
10            100 g of an  $\alpha, \omega$ -dihydroxypolydimethylsiloxane having a viscosity  $\eta$  of 175,000 mPa s at 25°C and a  $\bar{M}_n$  of 75,000 and containing 450 ppm of hydroxyl groups (0.0026 SiOH units per 100 g of polymer) are introduced into a reactor.

15            Anhydrous nitrogen is also introduced into this reactor and, with stirring, 1 g (0.0067 mol) of vinyltrimethoxysilane and 0.0160 g (0.0004 mol) of sodium hydroxide of formula NaOH are introduced at ambient temperature (25°C).

20            The mixture is allowed to react for 1 hour at a temperature of 25°C and is then neutralised with 0.218 g of silyl phosphate which has a phosphoric acid equivalent content of 12.5% and is prepared in accordance with Example 2 of French Patent 2,410,004.

25            After devolatilisation of the alcohol formed (under 16 x 133.32 pascals), an oil is obtained which has a viscosity  $\eta$  of 178,000 mPa s at 25°C.  $^1\text{H}$  NMR,  $^{29}\text{Si}$  NMR and IR analyses show that this oil is devoid of

silanol groups and that it has a structure of formula:



An intermediate determination shows that after a reaction time of 7 minutes there are already no longer any silanol groups.

5 COMPARATIVE EXAMPLE 2

The procedure is as in Example 1, changing only the amount of vinyltrimethoxysilane introduced: 5 g (0.034 mol), that is to say in excess.

10 After a reaction time of 1 hour at a temperature of 25°C, it is found that the silanol groups have disappeared, but the viscosity of the polymer obtained is no higher than 15,000 mPa s at 25°C.

15 The degradation reactions of the polymer containing functional groups have substantially reduced the viscosity of the latter.

EXAMPLE 3

20 The procedure is as in Example 1, replacing the sodium hydroxide introduced by 0.0080 g (0.00014 mol) of potassium hydroxide, of formula KOH, and neutralising the potassium hydroxide, after a reaction time of 1 hour, with 0.076 g of silyl

phosphate (12.5% expressed as phosphoric acid).

The oil obtained has a viscosity  $\eta$  of 120,000 mPa s at 25°C.

<sup>1</sup>H NMR, <sup>29</sup>Si NMR and IR analyses show that  
5 this oil is devoid of silanol groups.

#### COMPARATIVE EXAMPLE 4

The procedure is as in Example 1, replacing  
the sodium hydroxide by 0.0080 g (0.00014 mol) of  
potassium hydroxide and changing the amount of  
10 vinyltrimethoxysilane: 2.5 g(0.017 mol), that is to say  
in excess; and the potassium hydroxide being  
neutralised, after a reaction time of 1 hour, with  
0.076 g of silyl phosphate (12.5% expressed as  
phosphoric acid).

15 After a reaction time of 1 hour at a  
temperature of 25°C, it is found that the silanol  
groups have disappeared, but the viscosity of the  
polymer obtained is 20,000 mPa s at 25°C.

The degradation reactions of the polymer  
20 containing functional groups have substantially reduced  
the viscosity of the latter.

#### EXAMPLE 5

The procedure is as in Comparative Example 4,  
adding 2.5 g (0.017 mol) of methanol to the reaction  
25 mixture.

After a reaction time of 1 hour, the polymer  
obtained has a viscosity  $\eta$  of 140,000 mPa s at 25°C and  
the polymer is devoid of silanol groups.

EXAMPLE 6

The procedure is as in Example 1,  
introducing:

- 100 g of  $\alpha,\omega$ -dihydroxypolydimethylsiloxane,
- 5 - 2.5 g (0.017 mol) of vinyltrimethoxysilane  
(excess),
- 0.016 g (0.0004 mol) of sodium hydroxide, and
- 2.5 g (0.078 mol) of methanol.

The mixture is allowed to react for 1 hour  
10 and is then neutralised.

After devolatilisation of the excess  
vinyltrimethoxysilane and the alcohol, an oil is  
obtained which has a viscosity  $\eta$  of 128000 mPa s at  
25°C and a number-average molecular mass  $\bar{M}_n = 73,000$ .

15  $^1\text{H}$  NMR,  $^{29}\text{Si}$  NMR and IR analyses show that the  
introduction of functional groups into this oil is  
complete: absence of silanol groups.

COMPARATIVE EXAMPLE 7

The procedure is as in Example 6, not  
20 introducing methanol; there is therefore an excess of  
vinyltrimethoxysilane, this excess not being  
compensated for by the presence of at least one  
volatile alcohol.

25 After a reaction time of 1 hour at a  
temperature of 25°C, it is found that the silanol  
groups have disappeared, but the viscosity of the  
polymer obtained at 25°C is 50,000 mPa s, which is  
confirmed by the number-average molecular mass of said

polymer:  $\bar{M}_n = 59,000$ .

COMPARATIVE EXAMPLE 8

The procedure is as in Example 1, using the following amounts of reagents:

- 5 - 100 g of  $\alpha, \omega$ -dihydroxypolydimethylsiloxane
- 5 g (0.034 mol) of vinyltrimethoxysilane (excess),  
and
- 0.0110 g (0.0002 mol) of potassium hydroxide.

After a reaction time of 1 hour at 25°C, the  
10 mixture is neutralised with 0.107 g of silyl phosphate  
(12.5% of phosphoric acid).

The polymer obtained has a viscosity  $\eta$  of  
6400 mPa s at 25°C.

EXAMPLE 9

15 The procedure is as in Comparative Example 8,  
adding 5 g (0.034 mol) of methanol to the reaction  
mixture.

After a reaction time of 1 hour, the polymer  
obtained has a viscosity  $\eta$  of 104,000 mPa s at 25°C and  
20 is devoid of silanol groups.

COMPARATIVE EXAMPLE 10

The procedure is as in Example 1, using the following amounts of reagents:

- 100 g of  $\alpha, \omega$ -dihydroxypolydimethylsiloxane,
- 25 - 2.5 g (0.017 mol) of vinyltrimethoxysilane  
(excess), and
- 0.0110 g (0.002 mol) of potassium hydroxide.

After a reaction time of 1 hour at 25°C, the

mixture is neutralised with 0.107 g of silyl phosphate (12.5% of phosphoric acid).

The polymer obtained has a viscosity  $\eta$  of 20,000 mPa s at 25°C.

5 EXAMPLE 11

The procedure is as in Comparative Example 10, adding 2.5 g (0.054 mol) of ethanol, of formula  $C_2H_5OH$ , to the reaction mixture.

The polymer obtained has a viscosity  $\eta$  of 92,000 mPa s at 25°C and is devoid of silanol groups.

EXAMPLE 12

The procedure is as in Comparative Example 10, adding 5 g (0.083 mol) of propan-2-ol to the reaction mixture.

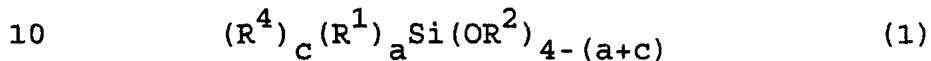
15 The polymer obtained has a viscosity  $\eta$  of 85,000 mPa s at 25°C and is devoid of silanol groups.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A process for the preparation of linear diorganopolysiloxane containing at least one alkoxy group bound to a silicon atom at each end of its chain, comprising the step of reacting the following compounds

5 - 100 parts, by weight, of at least one linear diorganopolysiloxane containing an hydroxy group bound to a silicon atom at each end of its chain,

- 0.35 to 6 parts, by weight, of at least one polyalkoxysilane of formula:



- 0.5 to 15 parts, by weight, of at least one alcohol, in the presence of a catalytically effective amount of sodium hydroxide or potassium hydroxide,

15 - wherein a is 0 or 1, or 2,

- wherein c is 0 or 1, or 2,

- wherein a + c = 0 or 1 or 2,

wherein R<sup>1</sup> represents a C<sub>1</sub> to C<sub>13</sub>

20 saturated or unsaturated, substituted or unsubstituted, aliphatic, cycloalkane or aromatic monovalent hydrocarbon radical.





25 - wherein  $R^2$  represents an aliphatic organic radical containing 1 to 8 carbon atoms, selected in particular from the alkyl radicals, alkylether radicals, alkylester radicals, alkylketone radicals, alkylcyano radicals, or an aralkyl radical containing 7 to 13 carbon atoms, and wherein if relevant more than one alkoxy group in the silane of formula (1) for  $R^2$ , may differ in the alkoxy groups, and

30 - wherein  $R^4$  represents a substituted or unsubstituted, saturated or unsaturated,  $C_1$  to  $C_{13}$  aliphatic, cycloalkane or aromatic monovalent hydrocarbon radical, and wherein  $R^4$  may optionally be identical to  $R^1$ .

35 2. A process according to claim 1 wherein the aromatic monovalent hydrocarbon radical can further comprise an epoxy, a primary, a secondary or tertiary amine mercapto group.

3. A process according to claim 1, wherein the quantity of at least one alcohol is between 2 and 5 parts by weight.

4. A process according to claim 1 comprising the steps of reacting one mole of at least one diorganopolysiloxane comprising a hydroxyl group linked to a silicon atom at each end of its chain with 2 to 6 moles of at least one



5 polyalkoxysilane of formula (I) in the presence of a catalytically effective quantity of sodium hydroxide or potassium hydroxide.

5. A process according to claim 4, wherein the sodium hydroxide or potassium hydroxide is in solution in an alcohol.

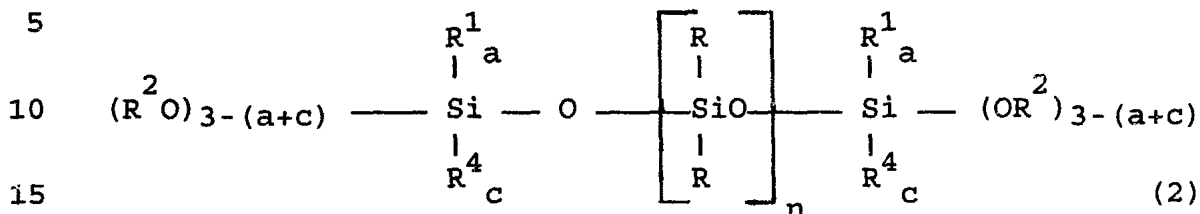
6. A process according to any one of the preceding claims wherein from 0.001 to 5 moles of sodium hydroxide or potassium hydroxide are used per one mole of silanol group =SiOH in the diorganopolysiloxane.

7. A process according to any one of the preceding claims, wherein the temperature is from -10°C and +90°C.

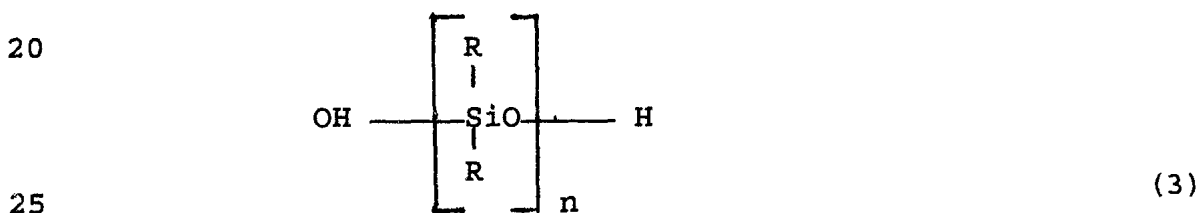
8. A process according to claim 7 wherein the temperature is from +10°C to 50°C.

9. A process according to claim 1 wherein the alcohol is methanol.

10. A process according to any one of the preceding claims, wherein the linear diorganopolysiloxane comprising at least one alkoxy group at each end of the chain has the formula:



and wherein the straight-chain diorganopolysiloxane comprising a hydroxyl group at each end of its chain has the formula



30

wherein the radicals R, which may be identical or different, represent monovalent hydrocarbon radicals having from 1 to 10 carbon atoms, which may be optionally substituted by halogen atoms or cyano groups, and

wherein n has a value sufficient to confer on the diorganopolysiloxanes of formula (2) and (3) a viscosity of 25 to 1,000,000 mPa s at 25°C.

11. A process according to claim 10 wherein the radical R in the formulae (2) and (3) is chosen from methyl, phenyl, vinyl and trifluoropropyl radicals.

12. A process according to any one of the preceding claims, wherein the polyalkoxysilane of formula (1) is chosen from methyltrimethoxysilane, methyltriethoxysilane, vinyltrimethoxysilane, tetraethoxysilane, vinyltriethoxysilane and methylvinyl dimethoxysilane.

13. A process according to any one of claims 10 to 12 wherein the step of reacting the product of formula (1) and the product of formula (3) for the introduction of functional groups is complete in less than 10 minutes.

14. A process according to claim 10 wherein at the end of the reaction, for the introduction of functional groups, between the product of formula (3) and the product of formula (1) the sodium hydroxide or potassium hydroxide used is neutralised.

15. A process according to claim 14 characterised in that the sodium hydroxide or potassium hydroxide is neutralised by silyl phosphate.



16. The product obtained according to one of claims 14  
to 15 for the preparation of single-component  
polysiloxane compositions which are stable on storage in  
the absence of moisture and which crosslink to form an  
5 elastomer in the presence of moisture.

17. A process for the preparation of straight-chain  
diorganopolysiloxane substantially as herein described  
with reference to any one of the examples, excluding the  
comparative examples.

DATED 27th July, 1993

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