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(73) Patenthaver: **Wacker Chemie AG, Hanns-Seidel-Platz 4, 81737 München, Tyskland**

(72) Opfinder: **SCHÖLEY, Peter, , 01665 Diera-Zehren OT Kleinzadel, Tyskland**
SCHEIM, Uwe, , 01640 Coswig, Tyskland

(74) Fuldmægtig i Danmark: **RWS Group, Europa House, Chiltern Park, Chiltern Hill, Chalfont St Peter, Bucks SL9 9FG, Storbritannien**

(54) Benævnelse: **TVÆRBINDELIGE MASSER BASERET PÅ ORGANOSILICIUMFORBINDELSER**

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Description

The invention relates to compositions crosslinkable by condensation reaction and based on organosilicon compounds, to processes for producing said compositions and to the use of same, and also to a process for producing organyloxy group-comprising organosilicon compounds.

One-component sealing compounds, which are storable with the exclusion of water and cure to give elastomers on ingress of water at room temperature with the elimination of alcohols, are already known. These products are used in large amounts, for example in the construction industry. These mixtures are often based on organopolysiloxanes bearing reactive substituents such as OH groups or hydrolysable groups, such as for example alkoxy groups. Furthermore, these sealing compounds may contain fillers, plasticizers, crosslinkers, catalysts and various additives.

In the case of compositions which cure by elimination of alcohol, an important step is what is known as the end-capping reaction. This term describes the reaction of terminal OH groups, in particular of linear organopolysiloxanes, with alkoxysilanes. Since it proceeds slowly, this reaction is typically effected in an upstream step prior to the production of the sealing compound. Various catalysts have been proposed for optimization of the reaction. For example, EP-B 1964872 describes the use of zinc chelates/the use of guanidines or lithium compounds.

Typically, however, such catalysts have to be removed from the reaction mixture or at least neutralized because of the reduction in the storage stability or because of their yellowing tendency. The disadvantage of this is that it requires an additional process step which is technically highly complex in particular due to the high polymer viscosities. EP-B 2176351 describes an alkoxy system in which the end-capping can be conducted without additional catalysts. The reactivity of the silane used, which has an alkyl group substituted in the alpha

position, is sufficiently high as to complete the end-capping within a few minutes.

However, it has been found these reactions result in a very large rise in the mixture viscosity. This is undesirable because such high viscosities are highly complex to handle industrially. Moreover, it is disadvantageous that subsequent processing steps such as the conveying with pumps or the incorporation of fillers, lead to undesirably strong temperature increases. This would reduce the storage stability of the RTV1 sealing compound produced, possibly additionally result in necessary cooling processes, and also risk the safety of the production plants due to the typically low flashpoints of the various mixture constituents.

DE 102007037196 A1, EP 1431330 A1 and EP 2789656 A1 each disclose organopolysiloxane compositions based on dihydroxydimethylpolysiloxanes and amino-functional silanes.

It was therefore an object to overcome the disadvantages of the prior art.

The invention provides compositions crosslinkable by condensation reaction, producible by mixing

(A) organosilicon compounds having at least two silanol groups and having a viscosity of 10^3 to 10^6 mPas at 25°C,

and

(M) mixtures containing
(B) organosilicon compounds of the formula

$$R^6R^7N\text{-}CR^1_2SiR_a(OR^2)_{3-a} \quad (I),$$

in which
R denotes identical or different monovalent hydrocarbon radicals,

R^1 denotes identical or different monovalent hydrocarbon radicals or a hydrogen atom,
R^2 may be identical or different and denotes monovalent, optionally substituted hydrocarbon radicals,
R^6 may be identical or different and denotes monovalent, optionally substituted hydrocarbon radicals or a hydrogen atom,
R^7 may be identical or different and denotes monovalent, optionally substituted hydrocarbon radicals, where R^6 and R^7 can also form a ring which may optionally be interrupted by heteroatoms,
and
a is equal to 0 or 1, preferably 0,
and/or the partial hydrolysates thereof,

component (C), selected from
(C2) compounds of the formula

$$R^5OH \qquad (III),$$

in which
R^5 may be identical or different and denotes monovalent, optionally substituted hydrocarbon radicals,
and
optionally (C1) organosilicon compounds of the formula $R^3_{4-b}Si(OR^4)_b$ (II), in which R^3 may be identical or different and denotes monovalent, SiC-bonded, optionally substituted hydrocarbon radicals which may be interrupted by oxygen atoms, excluding $R^6R^7N-CR^1_2-$ radicals, R^4 may be identical or different and denotes monovalent hydrocarbon radicals which may optionally be interrupted by oxygen atoms, and b is 2, 3 or 4, preferably 3 or 4, and optionally (D) catalyst.

The partial hydrolysates of the compounds of formula (I) may be partial homohydrolysates or also partial cohydrolysates. If the component (B) used according to the invention is partial hydrolysates of the compounds of the formula (I), preference is given to those having up to 10 silicon atoms.

Preferably, the radical R is optionally substituted, monovalent hydrocarbon radicals having 1 to 18 carbon atoms, particularly

preferably alkyl radicals, the vinyl radical, the 3,3,3-trifluoroprop-1-yl radical or the phenyl radical, in particular the methyl radical.

Examples of radicals R are alkyl radicals such as the methyl, ethyl, n-propyl, isopropyl, 1-n-butyl, 2-n-butyl, isobutyl, tert-butyl, n-pentyl, isopentyl, neopentyl, tert-pentyl radical; hexyl radicals such as the n-hexyl radical; heptyl radicals such as the n-heptyl radical; octyl radicals such as the n-octyl radical and isooctyl radicals such as the 2,2,4-trimethylpentyl radical; nonyl radicals such as the n-nonyl radical; decyl radicals such as the n-decyl radical; dodecyl radicals such as the n-dodecyl radical; octadecyl radicals such as the n-octadecyl radical; cycloalkyl radicals such as the cyclopentyl, cyclohexyl and cycloheptyl radical and methylcyclohexyl radicals; alkenyl radicals such as the vinyl, 1-propenyl and 2-propenyl radical; aryl radicals such as the phenyl, naphthyl, anthryl and phenanthryl radical; alkaryl radicals such as o-, m-, p-tolyl radicals, xylyl radicals and ethylphenyl radicals; and aralkyl radicals such as the benzyl radical and the α- and β-phenylethyl radicals.

Examples of radicals R^1 are a hydrogen atom and the radicals specified for R.

The radical R^1 is preferably a hydrogen atom and hydrocarbon radicals having 1 to 20 carbon atoms, in particular a hydrogen atom.

Examples of radicals R^2, R^4 and R^5 are independently of one another the radicals specified for R.

The radicals R^2, R^4 and R^5 are preferably independently of one another alkyl radicals having 1 to 8 carbon atoms, particularly preferably the methyl, ethyl, n-propyl or isopropyl radical, in particular the methyl or ethyl radical, very particularly preferably the ethyl radical.

The radicals R^2, R^4 and R^5 in the mixture (M) used according to the invention preferably have the same definition.

Examples of radicals R^6 are a hydrogen atom and the radicals specified for R.

The radical R^6 is preferably a hydrogen atom or linear, branched or cyclic hydrocarbon radicals having 1 to 6 carbon atoms, in particular the methyl, ethyl, n-butyl, cyclohexyl or phenyl radical.

Examples of radicals R^7 are the radicals specified for R.

The radical R^7 is preferably a hydrogen atom or linear, branched or cyclic hydrocarbon radicals having 1 to 6 carbon atoms, particularly preferably a hydrogen atom, the methyl, ethyl or n-butyl radical.

Radicals R^6 and R^7 may, together with the nitrogen atom to which they are attached, form a ring which for example may result in 1,4-tetrahydrooxazine or piperazine structures.

Examples of compounds (B) used according to the invention are aminomethyltriethoxysilane, N-methylaminomethyltriethoxysilane, N-ethylaminomethyltriethoxysilane, N-n-propylaminomethyltriethoxysilane, N-n-butylaminomethyltriethoxysilane, N-cyclohexylaminomethyltriethoxysilane, N-phenylaminomethyltriethoxysilane, N,N-dimethylaminomethyltriethoxysilane, N,N-diethylaminomethyltriethoxysilane, N,N-di-n-propylaminomethyltriethoxysilane, N,N-di-n-butylaminomethyltriethoxysilane, aminomethyltrimethoxysilane, N-methylaminomethyltrimethoxysilane, N-ethylaminomethyltrimethoxysilane, N-n-propylaminomethyltrimethoxysilane, N-n-butylaminomethyltrimethoxysilane, N-cyclohexylaminomethyltrimethoxysilane, N-phenylaminomethyltrimethoxysilane, N,N-dimethylaminomethyltrimethoxysilane, N,N-diethylaminomethyltrimethoxysilane, N,N-di-n-propylaminomethyltrimethoxysilane, N,N-di-n-butylaminomethyltrimethoxysilane, 4-(triethoxysilylmethyl)tetrahydro-1,4-oxazine and 4-

(trimethoxysilylmethyl)tetrahydro-1,4-oxazine, where N-cyclohexylaminomethyltriethoxysilane, N-phenylaminomethyltriethoxysilane, N,N-di-n-butylaminomethyltriethoxysilane, 4-(triethoxysilylmethyl)tetrahydro-1,4-oxazine or 4-(trimethoxysilylmethyl)tetrahydro-1,4-oxazine are preferred and N,N-di-n-butylaminomethyltriethoxysilane or 4-(triethoxysilylmethyl)tetrahydro-1,4-oxazine are particularly preferred.

The compounds (B) used according to the invention are commercial compounds or can be produced by standard chemical methods.

Examples of radicals R^3 are the radicals specified for R and also radicals substituted with amino groups, such as $H_2N(CH_2)_3-$, $H_2N(CH_2)_2NH(CH_2)_2-$, $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_3-$, $H_3CNH(CH_2)_3-$, $C_2H_5NH(CH_2)_3-$, $H_2N(CH_2)_4-$, $H_2N(CH_2)_5-$, $H(NHCH_2CH_2)_3-$, cyclo-$C_6H_{11}NH(CH_2)_3-$, $(CH_3)_2N(CH_2)_3-$ and $(C_2H_5)_2N(CH_2)_3-$ radicals.

The radical R^3 is preferably the methyl, n-butyl, 2,2,4-trimethylpentyl, n-hexadecyl, vinyl or phenyl radical or $H_2N(CH_2)_3-$, $H_2N(CH_2)_2NH(CH_2)_2-$ or cyclo-$C_6H_{11}NH(CH_2)_3-$ radicals.

Examples of compounds (C1) optionally used are methyltrimethoxysilane, ethyltrimethoxysilane, n-propyltrimethoxysilane, n-butyltrimethoxysilane, n-hexadecyltrimethoxysilane, vinyltrimethoxysilane, phenyltrimethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, n-propyltriethoxysilane, n-butyltriethoxysilane, n-hexadecyltriethoxysilane, vinyltriethoxysilane, phenyltriethoxysilane, tetraethoxysilane, 3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N-cyclohexyl-3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane and N-(2-aminoethyl)-3-aminopropyltriethoxysilane and N-cyclohexyl-3-aminopropyltriethoxysilane, where methyltrimethoxysilane, n-hexadecyltrimethoxysilane, vinyltrimethoxysilane, phenyltrimethoxysilane, methyltriethoxysilane, n-hexadecyltriethoxysilane, vinyltriethoxysilane, phenyltriethoxysilane, tetraethoxysilane, 3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N-cyclohexyl-3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, N-

(2-aminoethyl)-3-aminopropyltriethoxysilane or N-cyclohexyl-3-aminopropyltriethoxysilane are preferred and methyltriethoxysilane, vinyltriethoxysilane, phenyltriethoxysilane, tetraethoxysilane, 3-aminopropyltriethoxysilane, N-(2-aminoethyl)-3-aminopropyltriethoxysilane or N-cyclohexyl-3-aminopropyltriethoxysilane are particularly preferred.

The compounds (C1) optionally used are commercial compounds or can be produced by standard chemical methods.

Examples of compounds (C2) used according to the invention are methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutyl alcohol, sec-butyl alcohol, amyl alcohols, such as pentan-1-ol, pentan-2-ol, pentan-3-ol, *tert*-pentanol, 3-methylbutan-1-ol, 3-methylbutan-2-ol, 2,2-dimethyl-1-propanol, n-hexanol and n-octanol, methanol or ethanol being preferred and ethanol being particularly preferred.

The compounds (C2) used according to the invention are commercial compounds or can be produced by standard chemical methods.

The mixtures (M) used according to the invention contain component (C) in amounts of preferably 0.01 to 20 parts by weight, particularly preferably 0.05 to 5 parts by weight, in particular 0.1 to 1 part by weight, based in each case on 100 parts by weight of component (B).

The component (C) used according to the invention may be exclusively compounds (C2) or mixtures of compounds (C1) and (C2).

If the component (C) used according to the invention is mixtures of compounds (C1) and (C2), these are used in a weight ratio of (C1) to (C2) of preferably 0.01:1 to 1000:1.

The component (C) used according to the invention preferably is exclusively compounds (C2).

In a further preferred embodiment, the component (C) used according to the invention is mixtures of organosilicon compounds (C1) and compounds (C2) in a weight ratio of (C1) to (C2) of 100:1 to 1000:1.

The catalyst (D) optionally present in the mixtures (M) used according to the invention may be any known catalysts which have also been used to date in what are known as end-capping reactions.

Preferred examples of catalysts (D) are zinc acetylacetonate, lithium ethoxide, lithium methoxide, n-butyllithium, N,N-di-n-butylammonium formate, N,N-di-n-butylammonium acetate, N,N,N',N'-tetramethylguanidine or 1,5,7-triazabicyclo[4.4.0]dec-5-ene, particular preference being given to 1,5,7-triazabicyclo[4.4.0]dec-5-ene.

If the mixtures (M) used according to the invention contain catalyst (D), this involves amounts of by preference 0.001 to 1 part by weight, preferably 0.005 to 0.1 parts by weight, in each case based on 100 parts by weight of the mixture (M). The mixtures (M) preferably contain no catalysts (D).

The individual constituents of the mixture (M) used according to the invention may in each case be one kind of such a constituent or else a mixture of at least two different kinds of such constituents.

The mixtures (M) used according to the invention are preferably essentially composed of the components (B), (C) and optionally (D), and they particularly preferably are composed to an extent of at least 95% by weight of the components (B), (C) and optionally (D). In particular, the mixtures (M) used according to the invention do not contain any further constituents besides the components (B), (C) and optionally (D).

To prepare the mixtures (M) used according to the invention, all constituents can be mixed with one another in any sequence. This

mixing preferably takes place at room temperature and pressure of the surrounding atmosphere, that is to say about 900 to 1100 hPa and with the greatest possible exclusion of water from the surrounding atmosphere.

The compositions according to the invention contain mixtures (M) in amounts of preferably 1 to 10 parts by weight, particularly preferably 1 to 5 parts by weight, in particular 1.5 to 3.5 parts by weight, based in each case on 100 parts by weight of component (A).

The organosilicon compounds (A) used according to the invention may be any organosilicon compounds having at least two OH groups, which have also been used to date in compositions crosslinkable by condensation reaction.

The organosilicon compounds (A) used according to the invention are preferably those containing units of the formula

$$R^8_d(OH)_eSiO_{(4-d-e)/2} \qquad (IV),$$

in which
R^8 may be identical or different and denotes optionally substituted hydrocarbon radicals which may be interrupted by oxygen atoms,
d is 0, 1, 2 or 3, preferably 2, and
e is 1, 2 or 3, preferably 0 or 1,
with the proviso that the sum of d+e is ≤ 3 and at least two OH radicals are present per molecule.

Examples of radical R^8 are the examples specified for the R radical.

The radical R^8 is preferably monovalent hydrocarbon radicals having 1 to 18 carbon atoms, which are optionally substituted with halogen atoms, amino groups, ether groups, ester groups, epoxy groups, mercapto groups, cyano groups or (poly)glycol radicals, the latter being formed from oxyethylene and/or

oxypropylene units, particularly preferably is alkyl radicals having 1 to 12 carbon atoms, in particular is the methyl radical.

The organosilicon compounds (A) used according to the invention are particularly preferably essentially linear, OH-terminated organopolysiloxanes, in particular α,ω-dihydroxydialkylpolysiloxanes.

Preferred examples of organosilicon compounds (A) are $(HO)Me_2SiO[SiMe_2O]_{30-2000}SiMe_2(OH)$ with Me meaning methyl radical.

The organosilicon compounds (A) are commercial products or can be produced by standard methods in silicon chemistry.

Organosilicon compounds (A) used according to the invention have a viscosity of preferably 1000 to 500 000 mPas, particularly preferably 1000 to 350 000 mPas and in particular 5000 to 150 000 mPas at 25°C.

In the context of the present invention, the dynamic viscosity of the organosilicon compounds is preferably measured in accordance with DIN 53019. The procedure is preferably as follows: Unless otherwise stated, the viscosity is measured at 25°C using a "Physica MCR 300" rotational rheometer from Anton Paar. In this case, a coaxial cylinder measuring system (CC 27) with an annular measuring gap of 1.13 mm is used for viscosities of from 1 to 200 mPa·s, and a cone-plate measuring system (Searle system with CP 50-1 measuring cone) is used for viscosities of greater than 200 mPa·s. The shear rate is adapted to the polymer viscosity (1 to 99 mPa·s at 100 s^{-1}; 100 to 999 mPa·s at 200 s^{-1}; 1000 to 2999 mPa·s at 120 s^{-1}; 3000 to 4999 mPa·s at 80 s^{-1}; 5000 to 9999 mPa·s at 62 s^{-1}; 10 000 to 12 499 mPa·s at 50 s^{-1}; 12 500 to 15 999 mPa·s at 38.5 s^{-1}; 16 000 to 19 999 mPa·s at 33 s^{-1}; 20 000 to 24 999 mPa·s at 25 s^{-1}; 25 000 to 29 999 mPa·s at 20 s^{-1}; 30 000 to 39 999 mPa·s at 17 s^{-1}; 40 000 to 59 999 mPa·s at 10 s^{-1}; 60 000 to 149 999 at 5 s^{-1}; 150 000 to 199 999 mPa·s at 3.3 s^{-1}; 200 000 to 299 999 mPa·s at 2.5 s^{-1}; 300 000 to 1 000 000 mPa·s at 1.5 s^{-1}.

Component (A) can be mixed with the mixture (M) at temperatures preferably of between 5°C and 35°C and at a pressure preferably of between 0.1 bar and 300 bar. If desired, however, this mixing may also be effected at higher temperatures, for example temperatures in the range from 35 to 135°C. If desired, heating or cooling may be carried out.

The mixing according to the invention of component (A) with mixture (M) preferably takes place with the greatest possible exclusion of water from the surrounding atmosphere. This can be done, for example, in systems having no dead space. If the mixing is effected, for example, in open, batchwise-operating mixers, the greatest possible exclusion of moisture should be ensured, for example by blanketing with dry air or dry nitrogen.

During the mixing of the organosilicon compounds (A) with the mixture (M), a reaction of the OH groups in compound (A) with silanes (B) takes place. This forms silyl groups having hydrolysable groups on the polymer, meaning that crosslinked polymer structures can be formed on ingress of moisture. Under the above-described conditions in relation to temperature and pressure, the reaction times are preferably between 1 min and 30 min.

The mixing according to the invention can be effected with the aid of any desired mixing units, for example with static or dynamic mixers, with preference being given to dynamic mixers.

The mixing according to the invention is preferably conducted with continuously operating mixing units.

The invention provides a process for producing organyloxy group-comprising organosilicon compounds, characterized in that
(A) organosilicon compounds having at least two silanol groups and having a viscosity of 10^3 to 10^6 mPas at 25°C and
(M) mixtures containing (B) organosilicon compounds of the formula (I) and/or the partial hydrolysates thereof, component (C), selected from (C2) compounds of the formula (III), and

optionally (C2) organosilicon compounds of the formula (II), and optionally (D) catalyst
are mixed with one another and allowed to react.

The process according to the invention for producing organyloxy group-comprising organosilicon compounds has the advantage that the viscosity of the reaction mixture surprisingly rises only very moderately after the reaction has concluded.

It was also surprising that no yellowing occurred despite the presence of compounds (B) comprising amino groups.

In addition to the organosilicon compounds (A) and the mixtures (M), it is now possible to use, for the production of the compositions according to the invention, all substances which have also been used to date in compositions crosslinkable by condensation reaction, such as for example crosslinking catalysts (E), fillers (F), adhesion promoters (G), plasticizers (H), crosslinkers (J) and additives (K).

Examples of crosslinking catalysts (E) are the titanium compounds already known to date, such as tetraisopropoxytitanate, and also zirconium and hafnium compounds, zinc compounds such as zinc (2-ethylhexoate) and organic tin compounds, such as di-n-butyltin dilaurate and di-n-butyltin diacetate, di-n-butyltin oxide, dioctyltin diacetate, dioctyltin dilaurate, dioctyltin oxide and also reaction products of these compounds with alkoxysilanes such as tetraethoxysilane, with preference being given to di-n-octyltin oxide in tetraethyl silicate hydrolysate, di-n-octyltin oxide in a mixture of 50% by weight methyltriethoxysilane hydrolysate and 50% by weight 3-aminopropyltriethoxysilane, di-n-octyltin oxide in tetraisopropyl silicate and the reaction product of di-n-butyltin diacetate and tetraethoxysilane.

If the compositions according to the invention contain crosslinking catalysts (E), this involves amounts of by preference 0.0001 to 2 parts by weight, preferably 0.001 to 1 part by

weight, in each case based on 100 parts by weight of the composition according to the invention. The compositions according to the invention preferably contain catalyst (E).

Examples of fillers (F) are nonreinforcing fillers, i.e. fillers having a BET surface area of up to 50 m^2/g, such as quartz, diatomaceous earth, calcium silicate, zirconium silicate, zeolites, metal oxide powders such as oxides or mixed oxides of aluminum, titanium, iron or zinc, barium sulfate, calcium carbonate, gypsum, silicon nitride, silicon carbide, boron nitride, glass and plastic powder, such as polyacrylonitrile powder; reinforcing fillers, i.e. fillers having a BET surface area of more than 50 m^2/g, such as fumed silica, precipitated silica, precipitated calcium carbonate, carbon black such as furnace black and acetylene black, and silicon-aluminum mixed oxides of large BET surface area; fibrous fillers such as asbestos and plastic fibers. The fillers mentioned may be hydrophobicized, for example by treatment with organosilanes or organosiloxanes or by etherification of hydroxyl groups to alkoxy groups. If fillers (F) are used, they are preferably hydrophilic fumed silica, precipitated calcium carbonate and marble powder.

If the compositions according to the invention contain component (F), this involves amounts of by preference 1 to 80 parts by weight, preferably 5 to 65 parts by weight, in each case based on 100 parts by weight of composition according to the invention. The compositions according to the invention preferably contain component (F).

The adhesion promoter (G) optionally used in the compositions according to the invention may be silanes and organopolysiloxanes having functional groups, such as for example those having glycidoxypropyl, ureidopropyl or methacryloxypropyl radicals.

Examples of adhesion promoters (G) are epoxysilanes, such as glycidoxypropyltrimethoxysilanes, glycidoxypropylmethyldimethoxysilane, glycidoxypropyltriethoxysilane or glycidoxypropylmethyldiethoxysilane, tris[3-

(trimethoxysilyl)propyl]isocyanurate, 2-(3-triethoxysilylpropyl)maleic anhydride, N-(3-trimethoxysilylpropyl)urea, N-(3-triethoxysilylpropyl)urea, N-(trimethoxysilylmethyl)urea, N-(methyldimethoxysilylmethyl)urea, N-(3-triethoxysilylmethyl)urea, N-(3-methyldiethoxysilylmethyl)urea, O-methylcarbamatomethylmethyldimethoxysilane, O-methylcarbamatomethyltrimethoxysilane, O-ethylcarbamatomethylmethyldiethoxysilane, O-ethylcarbamatomethyltriethoxysilane, 3-methacryloxypropyltrimethoxysilane, methacryloxymethyltrimethoxysilane, methacryloxymethylmethyldimethoxysilane, methacryloxymethyltriethoxysilane, methacryloxymethylmethyldiethoxysilane, 3-acryloxypropyltrimethoxysilane, acryloxymethyltrimethoxysilane, acryloxymethylmethyldimethoxysilanes, acryloxymethyltriethoxysilane, acryloxymethylmethyldiethoxysilane and partial condensates thereof and also ethoxy-terminated 3-aminopropyl(methyl)silsesquioxane (CAS number 128446-60-6).

If the compositions according to the invention contain component (G), this involves amounts of by preference 0.01 to 10 parts by weight, preferably 0.1 to 2.5 parts by weight, in each case based on 100 parts by weight of the composition according to the invention. Except when using calcium carbonates as filler, the compositions according to the invention preferably contain no component (G). If the compositions according to the invention contain calcium carbonate as filler (F), preference is given to using component (G).

Examples of plasticizers (H) are room-temperature-liquid dimethylpolysiloxanes end-capped by trimethylsiloxy groups, in particular having viscosities at 25°C in the range between 5 and 10 000 mPas, and high-boiling hydrocarbons, such as paraffin oils or mineral oils consisting of naphthenic and paraffinic units.

If the compositions according to the invention contain component (H), this involves amounts of by preference 1 to 50 parts by weight, preferably 10 to 35 parts by weight, in each case based on 100 parts by weight of the composition according to the

invention. The compositions according to the invention preferably contain component (H).

The further crosslinkers (J) optionally used in the compositions according to the invention may be any crosslinkers known to date having at least three condensable radicals, such as for example silanes having three organyloxy groups that are different from component (B).

The further crosslinkers (J) optionally used in the compositions according to the invention are particularly preferably silane crosslinkers, such as tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, tetrabutoxysilane, methyltrimethoxysilane, methyltriethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, 1,2-bis(trimethoxysilyl)ethane, 1,2-bis(triethoxysilyl)ethane, methyltriacetoxysilane, ethyltriacetoxysilane, methyltris(methylethylketoximo)silane or vinyltris(methylethylketoximo)silane, and partial hydrolysates thereof.

The further crosslinkers (J) optionally used in the compositions according to the invention are commercial products or can be produced by methods known in silicon chemistry.

If the compositions according to the invention contain further crosslinkers (J), this involves amounts of by preference 0.1 to 10 parts by weight, particularly preferably 0.2 to 5 parts by weight, very particularly preferably 0.5 to 3 parts by weight, in each case based on 100 parts by weight of the composition according to the invention. The compositions according to the invention preferably contain crosslinkers (J).

If the mixture (M) used according to the invention already contains silanes (C1) of the formula (II) with b equal to 3 or 4, the use of crosslinker (J) can be dispensed with or the amount used can be reduced.

Examples of additives (K) are pigments, dyes, odorants, oxidation inhibitors, agents for influencing the electrical properties, such as conductive carbon black, flame retardants, light stabilizers and agents for prolonging the skin formation time, such as silanes having an SiC-bonded mercaptoalkyl radical, cell-generating agents, for example azodicarbonamide, heat stabilizers and thixotropic agents, such as for example polyethers, biocides such as fungicides, bactericides, acaricides and modulus-regulating agents such as polydimethylsiloxanes having just one OH end group and also agents for improving the storage stability, such as alkylphosphonic acids or phosphoric esters.

If the compositions according to the invention contain component (K), this involves amounts of by preference 0.0001 to 10 parts by weight, preferably 0.001 to 10 parts by weight, in each case based on 100 parts by weight of the composition according to the invention. The compositions according to the invention preferably contain component (K).

The compositions according to the invention are preferably those producible using
(A) organosilicon compounds,
(M) mixtures containing organosilicon compounds (B) and component (C) selected from compounds (C2) and optionally organosilicon compounds (C1), optionally catalyst (D),
optionally (E) crosslinking catalysts,
optionally (F) fillers,
optionally (G) adhesion promoters,
optionally (H) plasticizers,
optionally (J) crosslinkers and
optionally (K) additives.

The compositions according to the invention are particularly preferably those producible using
(A) essentially linear, OH-terminated organopolysiloxanes,
(M) mixtures containing organosilicon compounds (B) and compounds (C2), and optionally catalyst (D),
(E) crosslinking catalysts,

optionally (F) fillers,
optionally (G) adhesion promoters,
optionally (H) plasticizers,
optionally (J) crosslinkers and
optionally (K) additives.

Particular preference is given to producing the compositions according to the invention using no constituents beyond components (A) to (K).

The individual constituents of the compositions according to the invention may in each case be one kind of such a constituent or else a mixture of at least two different kinds of such constituents.

The present invention further provides a process for producing the compositions according to the invention, characterized in that
in a first step
organosilicon compounds (A) optionally in a mixture with plasticizer (H) and mixtures (M) are mixed with one another and allowed to react and
in a second step
the composition obtained in the first step is mixed with at least one component selected from crosslinking catalysts (E), fillers (F), adhesion promoters (G), plasticizers (H), crosslinkers (J) and additives (K).

The constituents can be mixed in the second step of the process according to the invention at temperatures preferably of between 5°C and 35°C and at a pressure preferably of between 0.1 bar and 300 bar. If desired, however, this mixing may also be effected at higher temperatures, for example temperatures in the range from 35 to 135°C. If desired, heating or cooling may be carried out.

Plasticizer (H) may be mixed entirely or partially with the polymer (A) as early as in the first step. The further components

(E) to (K) optionally used may be mixed in in any desired sequence in the second step of the process according to the invention.

For convenience of processing, further plasticizers (H), if not already fully mixed with the polymer (A) in the first step, adhesion promoters (G) and further silanes (J) are preferably first added, and then fillers (F) and lastly crosslinking catalyst (E) and further additives (K) are added.

The mixing according to the invention of the individual components preferably takes place with the greatest possible exclusion of water from the surrounding atmosphere, which can for example be realized by blanketing with dry air or dry nitrogen.

In addition, the point at which crosslinking catalyst (E) is added is generally unimportant. However, it is expedient to add the catalyst only at the end, since the mixture is then activated. In practice, those skilled in the art will wish to avoid excessively long mixing of sealing compounds that are already highly reactive, since the complete exclusion of moisture during the production of the mixture is difficult or at least uneconomical.

After all desired constituents have been mixed, the composition according to the invention is preferably degassed and filled into moisture-tight containers.

The production according to the invention of the crosslinkable compositions according to the invention may be conducted either batchwise or continuously, preference being given to the continuous mode of operation.

In the continuous mode of operation, organosilicon compound (A) is preferably first mixed with mixture (M) and the further components (E) to (K) are added after preferably at least 50%, particularly preferably at least 80%, of the OH groups of component (A) have reacted. Preferably, plasticizers (H), adhesion

promoters (G) and further silanes (J) are first added, then fillers (F) are mixed in and lastly crosslinking catalyst (E) and further additives (K) are added.

The compositions according to the invention are preferably one-component compositions which are storable with the exclusion of water and cure on ingress of water and which are generally referred to in the art as RTV-1 compositions.

The usual water content of air is sufficient for the crosslinking of the compositions according to the invention. The compositions according to the invention are preferably crosslinked at room temperature. They may, if desired, also be crosslinked at temperatures higher or lower than room temperature, for example at -5° to 15°C or at 30° to 50°C and/or using concentrations of water exceeding the normal water content of the air.

The crosslinking is preferably conducted at a pressure of from 100 to 1100 hPa, in particular at the pressure of the surrounding atmosphere.

The present invention further provides moldings produced by crosslinking the compositions according to the invention.

The compositions according to the invention can be used for all purposes for which it is possible to use compositions which are storable with the exclusion of water and crosslink to give elastomers on ingress of water at room temperature.

The compositions according to the invention thus have excellent suitability, for example, as sealants for joints, including vertical joints, and similar cavities of, for example, 10 to 40 mm internal width, for example of buildings, land vehicles, watercraft and aircraft, or as adhesives or cementing compositions, for example in window construction or in the production of aquariums or glass cabinets and, for example, for production of protective coatings, including those for surfaces exposed to the constant action of fresh or sea water, or coatings which prevent

sliding, or of elastomeric moldings and for the insulation of electrical or electronic devices.

The compositions according to the invention have the advantage that they are easy to produce and have a high storage stability over a long period of time.

The compositions according to the invention have the advantage that only small amounts of, if any, toxicologically dangerous cleavage products are produced.

The mixtures (M) according to the invention have the advantage that they can be further processed rapidly.

The mixtures (M) according to the invention have the advantage that organosilicon compound (B) does not generate any yellowing, in particular when it is present in the mixture with components (C1).

Furthermore, the compositions according to the invention have the advantage that they can be produced in a fully continuous manner.

In the examples described below, all viscosity data are based on a temperature of 25°C. Unless stated otherwise, the examples that follow are conducted at a pressure of the surrounding atmosphere, that is to say at around 1000 hPa, and at room temperature, that is to say at around 23°C, or at a temperature as results when combining the reactants at room temperature without supplemental heating or cooling, and at a relative humidity of about 50%. Due to the rapid mode of working in the laboratory, blanketing with dry air was omitted. In addition, unless otherwise stated, all reported parts and percentages relate to weight.

The viscosities hereinbelow were determined in accordance with DIN 53019 as described above.

The following components are used:

SB1: 4-(triethoxysilylmethyl)tetrahydro-1,4-oxazine

SB2: N-cyclohexylaminomethyltriethoxysilane

SB3: 4-(triisopropoxysilylmethyl)tetrahydro-1,4-oxazine

TES: tetraethoxysilane (commercially available under the name "TES 28" from Wacker Chemie AG, Munich, Germany)

VTMO: vinyltrimethoxysilane

GF93: 3-aminopropyltriethoxysilane

GF9: N-(2-aminoethyl)-3-aminopropyltriethoxysilane

Example 1

A mixture of 490 **g of an** α,ω-dihydroxypolydimethylsiloxane having a viscosity of 80 000 mPa·s (commercially available under the name "Polymer FD 80" from Wacker Chemie AG, Munich, Germany) and 94 **g of an** α,ω-bis(trimethylsiloxy)polydimethylsiloxane having a viscosity of 1000 mPa·s (commercially available under the name "Weichmacher 1000" from Wacker Chemie AG, Munich, Germany) was mixed with a mixture of 16.5 g of 4-(triethoxysilylmethyl)tetrahydro-1,4-oxazine (SB1) and 0.3 g of methanol. The viscosity of the polymer mixture thus obtained was measured after 24 hours of storage at room temperature and was 67 800 mPas.

Examples 2 to 16

The procedure described in example 1 was repeated, with the modification that the mixtures described in table 1 were used. The resulting viscosities are likewise given in table 1.

Comparative example 1

The procedure described in example 1 was repeated, with the modification that no methanol was used.

Table 1:

Example	**Mixture**			**Viscosity**
C1	16.8 g of SB1	-	-	107 000 mPas

1	16.5 g of SB1	-	0.30 g of methanol	67 800 mPas
2	16.5 g of SB1	-	0.15 g of ethanol	78 100 mPas
3	16.5 g of SB1	-	0.30 g of ethanol	78 000 mPas
4	16.5 g of SB1	-	0.60 g of ethanol	75 000 mPas
5	16.5 g of SB1	0.15 g of TES	-	78 500 mPas
6	16.5 g of SB1	0.30 g of TES	-	82 600 mPas
7	16.5 g of SB1	0.60 g of TES	-	82 300 mPas
8	16.5 g of SB1	0.15 g of VTMO	-	81 200 mPas
9	16.5 g of SB1	0.30 g of VTMO	-	82 600 mPas
10	16.5 g of SB1	0.60 g of VTMO	-	82 300 mPas
11	16.5 g of SB1	0.15 g of GF9	-	88 800 mPas
12	16.5 g of SB1	0.30 g of GF9	-	89 400 mPas
13	16.5 g of SB1	0.60 g of GF9	-	91 100 mPas
14	16.5 g of SB1	0.15 g of GF93	-	87 300 mPas
15	16.5 g of SB1	0.30 g of GF93	-	88 700 mPas
16	16.5 g of SB1	0.60 g of GF93	-	91 000 mPas

Examples E18, E20 and E21

The procedure described in example 1 was repeated, with the modification that the mixtures described in table 2 were used. The resulting viscosities are likewise given in table 2.

Comparative example 2

The procedure described in example 18 was repeated, with the modification that no VTMO was used.

Comparative example 3

The procedure described in example 20 was repeated, with the modification that no methanol was used.

Table 2:

Example	Mixture			Viscosity
C2	16.8 g of SB2	-	-	gelled
18	16.5 g of SB2	0.30 g of VTMO	-	81 400 mPas
C3	16.8 g of SB3	-	-	98 300 mPas
20	16.5 g of SB3	-	0.30 g of methanol	78 800 mPas
21	16.5 g of SB3	-	0.30 g of ethanol	78 000 mPas

Example 22

A mixture of 490 **g of an** α,ω-dihydroxypolydimethylsiloxane having a viscosity of 80 000 mPa·s (commercially available under the name "Polymer FD 80" from Wacker Chemie AG, Munich, Germany) and 94 **g of an** α,ω-bis(trimethylsiloxy)polydimethylsiloxane having a viscosity of 1000 mPa·s (commercially available under the name "Weichmacher 1000" from Wacker Chemie AG, Munich, Germany) was mixed in a planetary mixer with a mixture of 16.5 g of 4-(triethoxysilylmethyl)tetrahydro-1,4-oxazine and 0.3 g of methanol. After stirring this mixture for 30 min, 1 g of a product J1, which was composed of 16.0 mol% of units of the formula $MeSi(OEt)_2O_{1/2}$, 46.4 mol% of units of the formula $MeSi(OEt)O_{2/2}$, 36.5 mol% of units of the formula $MeSiO_{3/2}$, 0.2 mol% of units of the formula $Me_2Si(OEt)O_{1/2}$ and 0.9 mol% of units of the formula $Me_2SiO_{2/2}$, 8 g of 3-aminopropyltriethoxysilane (commercially available under the

name GENIOSIL® GF 93 from Wacker Chemie AG, Munich, Germany), 2 g of vinyltriethoxysilane (commercially available under the name GENIOSIL® GF 56 from Wacker Chemie AG, Munich, Germany) and 5 g of tetraethyl silicate (commercially available under the name "Silikat TES 28" from Wacker Chemie AG, Munich, Germany) were added and the mixture was mixed for a period of 5 minutes. 45 g of a fumed silica having a BET specific surface area of 150 m^2/g (commercially available under the name HDK® V15 from Wacker Chemie AG, Munich, Germany) were then mixed in and the mixture was completely homogenized at a pressure of 50 hPa. Lastly, 1 g of a 1:1 solution of octylphosphonic acid in methyltrimethoxysilane and 2 g of a reaction product of dibutyltin diacetate and tetraethoxysilane (commercially available under the name "Katalysator 41" from Wacker Chemie AG, Munich, Germany) were added and the mixture was homogenized for a further 5 min at a pressure of approx. 50 hPa (absolute). The RTV1 composition thus obtained was filled into commercially available moisture-tight polyethylene cartridges.

Product J1 was produced by hydrolysis and condensation of methyltriethoxysilane. At 25°C it had a density of 1.09 g/cm^3 and a viscosity of 28.4 mPa·s.

2 mm-thick sheets of the sealing compound produced in example 22 were in each case spread onto a polyethylene film, and after a day of curing were detached from the film and suspended such that air could be admitted from all sides for a further 6 days, such that the samples were cured over a total of 7 days. The relative humidity was set here at 50%, with the temperature being controlled at 23°C. Test specimens of the form S2 according to DIN 53504-85 were then stamped out of these sheets and the modulus of each was determined.

To determine the hardness, 6 mm-thick specimens were produced, which were cured on PE films over 7 days at a relative humidity of 50% and at a temperature of 23°C by reaction with the ambient atmospheric humidity.

The hardness of the sealing compound cured tack-free was 22 Shore A. The modulus (tensile stress value at 100% elongation) was determined to be 0.38 MPa. The sealing compound is thus of exceptional suitability for the sealing of building joints, for example.

Patentkrav

1. Masser, der kan tværbindes ved hjælp af kondensationsreaktion og kan fremstilles under anvendelse af
(A) organosiliciumforbindelser med mindst to silanolgrupper med en viskositet, der er bestemt efter metoden, der er angivet i beskrivelsen, fra 10^3 til 10^6 mPas ved 25°C, og
(M) blandinger, der indeholder
(B) organosiliciumforbindelser med formlen

$$R^6R^7N\text{-}CR^1_2SiR_a(OR^2)_{3-a} \qquad (I),$$

hvor
R betyder ens eller forskellige monovalente kulbrinterester,
R^1 betyder ens eller forskellige monovalente kulbrinterester eller brintatom,
R^2 kan være ens eller forskellig og betyder monovalente eventuelt substituerede kulbrinterester,
R^6 kan være ens eller forskellig og betyder monovalente eventuelt substituerede kulbrinterester eller brintatom,
R^7 kan være ens eller forskellig og betyder monovalente eventuelt substituerede kulbrinterester, hvor R^6 og R^7 også kan danne en ring, der eventuelt kan være afbrudt af heteroatomer, og
a er lig med 0 eller 1,
og/eller hvis delhydrolysater,
komponent (C), udvalgt fra
(C2) forbindelser med formlen

$$R^5OH \qquad (III),$$

hvor
R^5 kan være ens eller forskellig og betyder monovalente eventuelt substituerede kulbrinterester,
samt
eventuelt (D) katalysator.

2. Masser ifølge krav 1, kendetegnet ved, at resterne R^2, R^4 og R^5 har den samme betydning i den anvendte blanding (M).

3. Masser ifølge krav 1 eller 2, kendetegnet ved, at blandingerne (M) indeholder komponent (C) i mængder på 0,01 til 20 vægtdele i forhold til 100 vægtdele af komponent (B).

4. Masser ifølge et eller flere af kravene 1 til 3, kendetegnet ved, at det med hensyn til forbindelser (B) drejer sig om N-cyclo-hexylaminomethyltriethoxysilan, N-phenylaminomethyltriethoxysilan, N,N-Di-n-butylaminomethyltriethoxysilan, 4-(triethoxysilylmethyl)tetrahydro-1,4-oxazin eller 4-(trimethoxysilylmethyl)tetrahydro-1,4-oxazin.

5. Masser ifølge et eller flere af kravene 1 til 4, kendetegnet ved, at det drejer sig om masser, der kan fremstilles under anvendelse af
(A) organosiliciumforbindelser,
(M) blandinger, der indeholder organosiliciumforbindelser, (B) samt komponent (C), udvalgt fra forbindelser (C2), samt eventuelt katalysator (D),
eventuelt (E) tværbindingskatalysatorer,
eventuelt (F) fyldstoffer,
eventuelt (G) bindemidler,
eventuelt (H) blødgøringsmidler,
eventuelt (J) tværbindingsmidler og
eventuelt (K) additiver.

6. Fremgangsmåde til fremstilling af organosiliciumforbindelser, der indeholder organyloxygrupper, kendetegnet ved, at
(A) organosiliciumforbindelser med mindst to silanolgrupper med en viskositet, der er bestemt i henhold til metoden, der er angivet i beskrivelsen, fra 10^3 til 10^6 mPas ved 25°C og
(M) blandinger, der indeholder (B) organosiliciumforbindelser med formlen (I), og/eller delhydrolysater af disse, komponent (C), udvalgt fra (C2) forbindelser med formlen (III), samt eventuelt (D) katalysator
blandes og reagerer med hinanden.

7. Fremgangsmåde til fremstilling af masser ifølge et eller flere af kravene 1 til 5, kendetegnet ved, at
i et 1. trin

organosiliciumforbindelser (A), eventuelt blandet med blødgøringsmiddel (H) og blandinger (M) blandes og reagerer med hinanden og

i et 2. trin

sammensætningen, der er opnået i 1. trin, blandes med mindst én komponent, udvalgt fra tværbindingskatalysatorer (E), fyldstoffer (F), bindemidler (G), blødgøringsmidler (H), tværbindingsmidler (J) og additiver (K).

8. Formlegeme, fremstillet ved tværbinding af sammensætningerne ifølge et eller flere af kravene 1 til 5, eller fremstillet ifølge krav 6 eller 7.