(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
28 January 2010 (28.01.2010)

PCT

(10) International Publication Number
WO 2010/009752 A1

(51) International Patent Classification:
C08L 83/04 (2006.01) *C08K 5/524* (2006.01)

(21) International Application Number:
PCT/EP2008/059513

(22) International Filing Date:
21 July 2008 (21.07.2008)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant *(for all designated States except US)*: **MOMENTIVE PERFORMANCE MATERIALS GMBH** [DE/DE]; Gebäude V 7, 51368 Leverkusen (DE).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **STEINBERGER, Helmut** [DE/DE]; Winand-Rossi-Strasse 36, 51373 Leverkusen (DE). **MARCINIEC, Bogdan** [PL/PL]; Wilkonskich 13, PL-62-020 Swarzedz (PL). **KOWNACKI, Ireneusz** [PL/PL]; Ogrodowa 2, PL-62-430 Powidz (PL).

(74) Agent: **ROOS, Peter**; Gille Hrabal Struck Neidlein Prop Roos, Brucknerstr. 20, 40593 Düsseldorf (DE).

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

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

WO 2010/009752 A1

(54) Title: CURABLE SILICONE COMPOSITIONS COMPRISING CYCLO-ALKYLPHOSPHITES

(57) Abstract: The present invention relates to hydrosilylation-curing polyorganosiloxane compositions and/or silane compositions comprising phosphites, transition metal compounds comprising phosphite ligands, cured products prepared from the hydrosilylation-curing polyorganosiloxane compositions and/or silane compositions and new phosphites.

CURABLE SILICONE COMPOSITIONS COMPRISING CYCLOALKYLPHOSPHITES

The present invention relates to hydrosilylation-curing polyorganosiloxane compositions and/or silane compositions comprising phosphites, transition metal compounds comprising phosphite ligands, cured products prepared from the hydrosilylation-curing polyorganosiloxane compositions and/or silane compositions and new phosphites. In particular, the invention is related to transition metal compounds comprising polycycloaliphatic phosphites and the use of those phosphites as inhibitors in hydrosilylation curing silicone compositions.

Platinum (0)-vinylsiloxane complexes such as the divinyltetramethyl-disiloxane complex (Karstedt's catalyst) or tetravinyltetramethyl-cyclotetrasiloxane can catalyse the hydrosilylation reaction at very high reaction rates. Therefore these catalysts are currently used for crosslinking, curing or vulcanization of silicone rubber having alkenyl and SiH-groups by hydrosilylation between 20-200 °C. However, this reaction at room temperature according to Arrhenius Law sometimes shortens the pot-life or bath-life time in an unacceptable manner (1-10 min at 25 °C).

It is well known from prior art disclosures that the high reaction rates of platinum catalysts can be slowed down by inhibitors, such as esters, e.g. maleates and fumarates, ketones, sulfoxides, phosphines, phosphites, nitrogen- or sulphur containing derivatives, hydroperoxides as well as acetylene derivatives such as alkinoles. If one describes the effect of such inhibitors in terms of Arrhenius Law one can observe in generally a shifted line in a diagram showing 1/k (k=reaction constant [s^{-1}]) over 1/T (°K) as x-axis, i.e. if the pot-life is extended one can observe at the same time a decreased reaction rate at higher temperatures.

Some prior art documents attempt to decouple the effect of pot-life and cure rate at higher temperature. For example US 3,188,300 discloses specific aliphatic, cyclo-aliphatic and aromatic phosphites in order to anticipate premature gelling at 20 – 30 °C. EP 948565 A1 discloses siloxane compositions comprising substituted and aromatic phosphites, which shows a different relation between cure rate at 140 °C and pot-life at room temperature. US 2006/0135689 (Fehn) discloses siloxane compositions comprising olefin-nitrogen containing-ligand-platinum complexes, which should have enlarged pot-life at room temperature and high reaction rates at higher temperatures.

US 2006/0128881 A1 and US 2004/0116561 A1 disclose hydrosilylation curing polyorganosiloxane compositions comprising phosphites but fail to discloses phosphites having polycycloaliphatic groups. Moreover these documents are not concerned with the technical object of decoupling the effect of pot-life and cure rate at higher temperature in hydrosilylation curing polyorganosiloxane compositions.

US 3,188,300 A1 and US 5,380,812 also disclose the use of phosphite inhibitors as inhibitors in hydrosilylation curing silicone compositions. Among the possible substituents there are also mentioned monocycloaliphatic groups, i.e. cyclohexyl. The present inventors have found however, that the use of tris(cyclohexyl) phosphite reveals an unacceptable low curing rate at high temperatures, although the pot-life or storage stability, respectively, is acceptable.

Therefore, the present invention attempts to provide hydrosilylation curing polyorganosiloxane compositions, in particular, ´one-part´ hydrosilylation curing polyorganosiloxane compositions that have a long pot-life, i.e. storage stability, and at the same time have high curing rates at high temperatures, which property is not affected upon long-term storage. The present inventors have found that surprisingly phosphites having polycycloaliphatic substituents are suitable to solve these problems.

Accordingly the present invention is related to hydrosilylation-curing polyorganosiloxane compositions and/or silane compositions, comprising one or more phosphites having the formula:

$P(OR)_3$, (I),

wherein R is an organic group, and at least one group R is an aliphatic group comprising at least one substituted or unsubstituted polycycloaliphatic group. A polycycloaliphatic group comprises preferably more than one, preferably two to four, more preferably two or three rings, preferably carbon rings, which are preferably condensed which each other, that is, they share two carbon atoms.

The optional substituent groups may be located in particular at the polycycloaliphatic group. For example it may carry 1 to 3 exocyclic substituents, which are preferably selected from the group consisting of (C_1-C_3)-alkyl, (C_1-C_3)-alkoxy, halogen, cyano, (C_1-C_3)-alkoxycarbonyl, (C_1-C_3)-acyloxy. Preferably the aliphatic group comprising at least one substituted or unsubstituted polycycloaliphatic group has no substituents groups, that is, it consists solely of the polycycloaliphatic group and optionally an alkylene linking group, that links the polycycloaliphatic group with the oxygen atom.

In the phosphites used according to the invention preferably all of the groups R are aliphatic groups comprising at least one polycycloaliphatic group.

In the preferred phosphites used according to the invention the aliphatic group comprising at least one polycycloaliphatic group is a group of the formula (II):

$-(CH_2)_x$-A, (II)

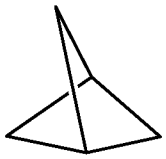
wherein x is 0, 1 or 2 and A is a polycycloaliphatic group.

The polycycloaliphatic group is, in particular, a saturated or unsaturated group, preferably a saturated group. The polycycloaliphatic group is preferably a bi- or tricyclic group. Preferably the polycycloaliphatic group has from 5 to 30 carbon atoms, more preferably from 5 to 20, still more preferably from 7 to 10 carbon atoms. Particularly preferred polycycloaliphatic groups are selected from the group consisting of:

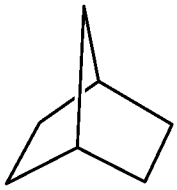
bicyclopentyl,
bicyclohexyl,
bicycloheptyl,
bicyclooctyl,
bicyclononyl,
bicyclodecyl,
tricyclopentyl,
tricyclohexyl,
tricycloheptyl,
tricyclooctyl,
tricyclononyl, and
tricyclodecyl,

which may have 1 to 3 exocyclic substituents, which are preferably selected from the group consisting of (C_1-C_3)-alkyl, (C_1-C_3)-alkoxy, halogen, cyano, (C_1-C_3)-alkoxycarbonyl, (C_1-C_3)-acyloxy. Preferably the polycycloaliphatic groups have no exocyclic substituents, that is, the skeleton carbon atoms solely constitute them.

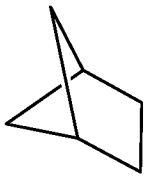
The polycycloaliphatic groups indicated before comprise all available isomers, including for example:



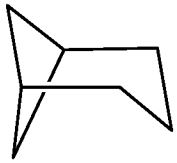
Bicyclo[1.1.1]pentane



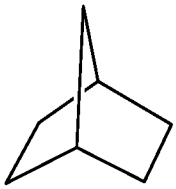
Bicyclo[2.2.1]heptane



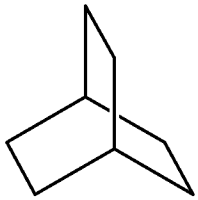
Bicyclo[2.1.1]hexane



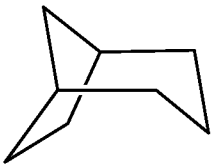
Bicyclo[3.1.1]heptane



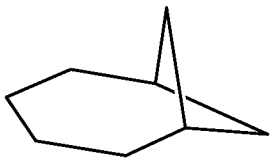
Bicyclo[2.2.1]heptane



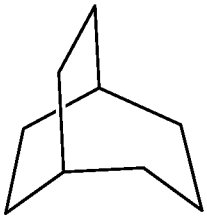
Bicyclo[2.2.2]octane



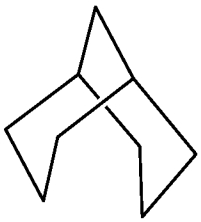
Bicyclo[3.2.1]octane



Bicyclo[4.1.1]octane



Bicyclo[3.2.2]nonane



Bicyclo[3.3.1]nonane

Furthermore preferred phosphites are those wherein the polycycloaliphatic group is connected via a (C_1-C_2)-alkylene group to oxygen atom that is attached to the phosphorous atom. Those polycycloaliphatic groups are preferably selected from the group, consisting of:

bicyclopentylmethyl,
bicyclohexylmethyl,
bicycloheptylmethyl,
bicyclooctylmethyl,
bicyclononylmethyl,
bicyclodecylmethyl,
tricyclopentylmethyl,
tricyclohexylmethyl,
tricycloheptylmethyl,
tricyclooctylmethyl,
tricyclononylmethyl, and
tricyclodecylmethyl,

which may have 1 to 3 exocyclic substituents that are attached to the cycloaliphatic moiety (that is not the connecting methylen bridge). With respect to the substituents it can be referred to the explanations given for the polycycloaliphatic group above.

Particularly preferred polycycloaliphatic groups are selected from the group consisting of:

bicyclo[2.2.1]hept-2-yl,
bicyclo[2.2.1]hept-2-yl-methyl,
adamantan-1-yl,
adamantan-2-yl,
adamantan-1-yl-methyl,
adamantan-2-yl-methyl, and

(+)- and/or (-)-isobornyl.

Particularly preferred phosphites have three groups OR, wherein all groups R are aliphatic groups comprising at least one substituted or unsubstituted polycyclo-aliphatic group. Particularly preferred phosphites are selected from the group consisting of:

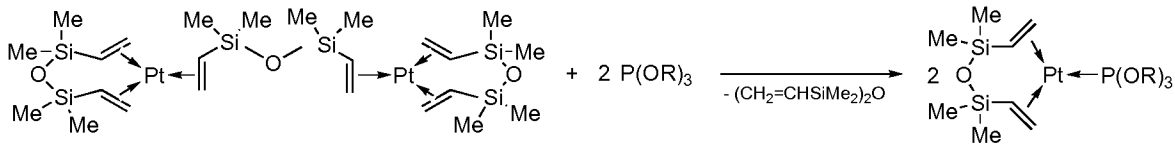
tris{bicyclo[2.2.1]hept-2-yl} phosphite,
tris{bicyclo[2.2.1]hept-2-ylmethyl} phosphite,
tris{adamantan-1-yl} phosphite,
tris{adamantan-2-yl} phosphite,
tris{adamantan-1-ylmethyl} phosphite,
tris{adamantan-2-ylmethyl} phosphite, and
tris{(+)- and/or (-)-isobornyl} phosphite,

among which tris{bicyclo[2.2.1]hept-2-yl} phosphite and tris{adamantan-1-yl} phosphite are known phosphites.

The inhibiting activity of the phosphites in the transition metal catalyzed hydrosilylation reaction is a consequence of the complex formation of the phosphites and the transition metal compound. Thus the present invention in a further aspect is also related to transition metal compounds, comprising at least one of the phosphites according to the invention. The transition metal in such transition metal compounds is preferably selected from group consisting of nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum, with platinum being the most preferred transition metal compound. Although it is possible to isolate transition metal compounds having those specific phosphite ligands of the invention, in the practice of hydrosilylation curing polyorganosiloxane systems, in general, certain common transition metal compounds are added together with the phosphites to the polyorganosiloxanes without separate formation of the transition metal phosphite complex compounds, or alternatively certain transition metal compounds are reacted with the phosphites so to say ´in situ´, the reaction product being added to the

hydrosilylation curing polyorganosiloxane systems. So from a technical point of view the isolation of the transition metal phosphite complex compounds has normally no importance and it suffices to determine the influence of the addition of the phosphites on the pot-life or storage stability and the curing rates at higher temperatures without identifying exactly the catalytically active transition metal species.

Nevertheless one can prepare and isolate on the other hand the underlying transition metal compounds of the phosphites of the invention by commonly known ligand exchange reactions. For example the well-known Karstedt catalyst can be reacted with the phosphites of the present invention to give the transition metal compounds in accordance with the present invention: The synthesis follows a pathway in that by example the well-known divinyl-tetramethyldisiloxane (´DVTMDS´) -bridged binuclear platinum complex (Karstedt's catalyst) can be cleaved by any nucleophile (e.g. phosphite), giving a mononuclear platinum complexes, according to equation:



In another aspect of the present invention it relates to the use of one or more phosphites according to the invention for the manufacture of hydrosilylation-curing polyorganosiloxane and/or silane compositions, and in particular the use of one or more as inhibitors of the hydrosilylation reaction in the curing of polyorganosiloxane compositions and/or silane compositions. Furthermore the invention relates to polyorganosiloxane and/or silane compositions curable by hydrosilylation comprising at least one or more of the phosphites according to the invention, the preferred ones given above.

The invention moreover relates to hydrosilylation-curing polyorganosiloxane compositions and/or silane compositions, comprising:

(A) one or more polyorganosiloxanes and/or silanes having in average at least two alkenyl groups,

(B) one or more polyorganosiloxanes and/or silanes having in average at least two SiH groups,

(C) one or more transition metal compounds, wherein the transition metal is selected from group consisting of nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum,

(D) one or more of the phosphites as defined in formula (I), and

(E) optionally one or more auxiliary agents.

Component (A):

The inventive composition comprises one or more polyorganosiloxanes and/or silanes having in average at least two alkenyl groups (A) e.g. those disclosed in US 3,096,303, US 5,500,148 A (examples). Suitable compounds (A) can be described by the general formula (III),

$$[M_aD_bT_cQ_d]_m \qquad (III)$$

wherein the formula (III) represents the ratios of the siloxy units M,D,T and Q, which can be distributed blockwise or randomly in the polymer chain. Within a polysiloxane chain each siloxane unit can be identical or different and preferably

a = 1-10

b = 0 -12000

c = 0 - 50

d = 0 - 1

m = 1- 5000.

These indices should represent the average polymerisation degree P_n based on the average number molecular mass M_n.

The polymer (A) is preferably selected from the group of alkenyl-containing polyorganosiloxanes, which can undergo hydrosilylation reactions with hydrogen siloxanes to form silicon carbon bonds.

The polymer (A) or mixtures thereof comprise groups selected from

M= $R_3SiO_{1/2}$, or M*

D= $R_2SiO_{2/2}$, or D*

T= $RSiO_{3/2}$, or T*

Q=$SiO_{4/2}$,

divalent R^2-groups,

wherein M*= $R^1_pR_{3-p}SiO_{1/2}$, D*= $R^1_qR_{2-q}SiO_{2/2}$, T*= $R^1SiO_{3/2}$,

wherein

p= 1-3,

q= 1-2.

R is preferably selected from n-, iso, or tertiary C_1-C_{30}-alkyl, alkoxyalkyl, C_5-C_{30}-cyclic alkyl, or C_6-C_{30}-aryl, alkylaryl, which groups can be substituted by one or more O-, N-, S- or F-atom, e.g. ethers or amides or poly(C_2 –C_4)-alkylene ethers with up to 1000 alkylene oxy units.

Examples of said monovalent residues R in component (A) include hydrocarbon groups and halohydrocarbon groups.

Examples of suitable monovalent hydrocarbon radicals include alkyl radicals, preferably such as CH_3-, CH_3CH_2-, $(CH_3)_2CH$-, C_8H_{17}- and $C_{10}H_{21}$-, cycloaliphatic radicals, such as cyclohexylethyl, aryl radicals, such as phenyl, tolyl, xylyl, aralkyl

radicals, such as benzyl and 2-phenylethyl. Preferable monovalent halohydrocarbon radicals have the formula $C_nF_{2n+1}CH_2CH_2$- wherein n has a value of from 1 to 10, such as, for example, $CF_3CH_2CH_2$-, $C_4F_9CH_2CH_2$- , $C_6F_{13}CH_2CH_2$-, C_2F_5–$O(CF_2$–CF_2–$O)_{1\text{-}10}CF_2$–, $F[CF(CF_3)$–CF_2–$O]_{1\text{-}5}$–$(CF_2)_{0\text{-}2}$–, C_3F_7–$OCF(CF_3)$– and C_3F_7–$OCF(CF_3)$–CF_2–$OCF(CF_3)$–.

Preferred groups for R are methyl, phenyl, 3,3,3-trifluoropropyl.

R^1 is selected from unsaturated groups, comprising C=C-group-containing groups (alkenyl groups), e.g.: n-, iso-, tertiary- or cyclic- C_2-C_{30}-alkenyl, C_6-C_{30}-cycloalkenyl, C_8-C_{30} -alkenylaryl, cycloalkenylalkyl, vinyl, allyl, methallyl, 3-butenyl, 5-hexenyl, 7-octenyl, ethyliden-norbornyl, styryl, vinylphenylethyl, norbornenyl-ethyl, limonenyl, substituted by one or more O- or F-atoms, e.g. ethers, amides or C_2–C_4-polyethers with up to 1000 polyether units. The alkenyl radicals are preferable attached to terminal silicon atoms, the olefin function is at the end of the alkenyl group of the higher alkenyl radicals, because of the more ready availability of the alpha-, omega-dienes used to prepare the alkenylsiloxanes.

Preferred groups for R^1 are vinyl, 5-hexenyl.

R^2 includes for example divalent aliphatic or aromatic n-, iso-, tertiary- or cyclo-C_1-C_{14}-alkylene, arylene or alkylenearyl groups which brigde siloxy units. Their content does not exceed 30 mol.% of all siloxy units. Preferred examples of suitable divalent hydrocarbon groups R^2 include any alkylene residue, preferably such as –CH_2-, -CH_2CH_2-, -$CH_2(CH_3)CH$-, -$(CH_2)_4$-, -$CH_2CH(CH_3)CH_2$-, -$(CH_2)_6$-, -$(CH_2)_8$- and -$(CH_2)_{18}$-; cycloalkylene radical, such as cyclohexylene; arylene radicals, such as phenylene, xylene and combinations of hydrocarbon radicals, such as benzylene, i.e. –CH_2CH_2–C_6H_4–CH_2CH_2–, –$C_6H_4CH_2$–. Preferred groups are alpha, omega-ethylene, alpha, omega-hexylene or 1,4-phenylene.

Examples of suitable divalent halohydrocarbon radicals R^2 include any divalent hydrocarbon group wherein one or more hydrogen atoms have been replaced by halogen, such as fluorine, chlorine or bromine. Preferable divalent halohydrocarbon residues have the formula $–CH_2CH_2(CF_2)_{1-10}CH_2CH_2-$ such as for example, $-CH_2CH_2CF_2CF_2CH_2CH_2-$ or other examples of suitable divalent hydrocarbon ether radicals and halohydrocarbon ether radicals including $–CH_2CH_2OCH_2CH_2-$, $-C_6H_4-0-C_6H_4-$, $-CH_2CH_2CF_2OCF_2CH_2CH_2-$,and $-CH_2CH_2OCH_2CH_2CH_2-$.

Such polymers containing R, R^1 and/or R^2 radicals are polyorganosiloxanes, e.g. alkenyl-dimethylsiloxy or trimethylsiloxy terminated polydimethylsiloxanes, which can contain other siloxane units than alkenylmethylsiloxy groups dimethylsiloxy groups such as poly-(dimethyl-co-diphenyl)siloxanes.

Broadly stated component (A) of the compositions of this invention can be any polyorganosiloxane compound containing two or more silicon atoms linked by oxygen and/or divalent groups R^2 wherein the silicon is bonded to 0 to 3 monovalent groups per silicon atom, with the proviso that the organosilicon compound contains at least two silicon-bonded unsaturated hydrocarbon residues. This component can be a solid or a liquid, free flowing or gum-like i.e. it has measurable viscosity of less than 100 kPa.s at a shear rate of $D=1\ s^{-1}$ at 25 °C.

The siloxane units with radicals R and/or R^1 can be equal or different for each silicon atom. In a preferred version the structure is represented by the general formulas (IIIa) to (IIIb), shown below.

One preferred polyorganosiloxane component (A) for the composition of this invention is a substantially linear polyorganosiloxane (A) having the formula (IIIa) or (IIIe) to (IIIi). The expression “substantially linear” includes polyorganosiloxanes that contain not more than 0.2 mol.% (trace amounts) of siloxy units of the type T or Q. This means the polymer (A) is preferably a linear, flowable fluid or gum (A1) with a Newton like viscosity but not solid at 25 °C.

$R^1_pR_{3-p}SiO(R_2SiO)_bSiR_{3-p}R_p^1$ (IIIa) (A1)

$R^1_pR_{3-p}(R_2SiO)_{b1}(R^1_qR_{2-q}SiO)_{b1x}SiR_{3-p}R_p^1$ (IIIb)

b = > 0 - 12000

b1 = > 0 -12000

b1x = 0 -1000

b1 + b1x = > 0 - 12000

p= 0 to 3

q= 1 to 2,

with the proviso, that there are at least two alkenyl groups per molecule.

Preferred groups for R are methyl, phenyl, 3,3,3-trifluoropropyl

Preferred groups for R^1 are vinyl, hex-5-enyl and cyclohexenyl-2-ethyl

The average polymerization degrees P_n or ´b´ etc. is based on M_n as average number molecular mass in the range of up to 12000, the preferred range is 500 to 5000. The viscosity of such polymers is in the range of 10 to 100,000,000 mPa.s at 25 °C at a shear rate of D=1 s^{-1}, the preferred range is about 200 to 10,000,000 mPa.s. Such a viscosity at 25 °C for the component (A) is suitable for the application of the manufacturing of broad variety of products such as molded or extruded shaped rubber parts with liquid silicone rubbers and high viscous rubbers, curable ´Formed-in-Place´- sealants well as coatings of substrates.

In the group of alkenyl comprising siloxanes (A) the addition of other so-called vinyl rich polymers (A2) is preferred in order to modify mechanical properties.

The polymers (A2) are selected either from the group consisting of polymers of the formulas (IIIb) to (IIId) or (IIIh) to (IIIi), i.e. linear polyorganosiloxanes having

additional alkenyl side groups or branched polyorganosiloxanes having a higher concentration of T- and Q-groups than the previous types.

$Me_3SiO(Me_2SiO)_{b1}(MeViSiO)_{b1x}SiMe_3$ (IIIc) ,and

$ViMe_2SiO(Me_2SiO)_{b1}(MeViSiO)_{b1x}SiMe_2Vi$ (IIId), whereby

Vi= vinyl.

The preferred value of b1x is less than 0.5 * b1 or zero. If b1x is not zero then it is preferably between 0.0003*b1 to 0.25*b1 preferably 0.0015*b1 to 0.15*b1.

Other preferred structures according of the formulas (IIIe) to (IIIi) achieve suitable viscosities as defined lateron and describe polymers applicable without any solvent for a viscosity adjustment. The range of subindices defines a range of the possible average polymerization degrees P_n.

$Vi_pMe_{3-p}SiO(Me_2SiO)_{10-12000}SiMe_{3-p}Vi_p$ (III e)

$PhMeViSiO(Me_2SiO)_{10-12000}SiPhMeVi$ (III f),

$Vi_pMe_{3-p}SiO(Me_2SiO)_{10-12000}(MeViSiO)_{1-2500}SiMe_{3-p}Vi_p$ (III g),

$Me_3SiO(Me_2SiO)_{10-12000}(MeViSiO)_{1-2500}SiMe_3$ (III h),

$PhMeViSiO(Me_2SiO)_{10-12000}(MePhSiO)_{1-1000}SiPhMeVi$ (III i) and

wherein Ph= phenyl,

p= 0 to 3, preferred p=1.

In a preferred embodiment the polymer component (A) is a mixture of polymers of the formula (IIIa) and of the formula (IIIb) whereby (IIIb) has an alkenyl content of 1 to 50 mol.% in a ratio in which the alkenyl content of mixture of (A1) and (A2) is below 2 mol.%.

Another class of preferred polymers are branched polyorganosiloxanes (A2) having a high concentration of $SiMe_{(3-p)}(alkenyl)_p$ groups with distinct cure rates. Such structures are especially used in release coating applications. Branched polymers are decribed e.g. in US 5,616,672 and are preferably selected from those of the

formula (III) wherein the polyorganosiloxane (A2) comprising alkenyl groups has more than 0.2 mol.% of $T=RSiO_{3/2}$ or $Q=SiO_{4/2}$-units.

Preferably the branched vinyl-rich polymers have a range of D : T > 10 : 1 preferably > 33 : 1 and/or respectively $(M^{alkenyl} : Q) = 0.6 - 4 : 1$.

All these polymers can be prepared by any of the conventional methods for preparing triorganosiloxane-terminated polydiorganosiloxanes. For example, a proper ratio of the appropriate hydrolyzable silanes, e.g., vinyldimethylchlorosilane and dimethyldichlorosilane, may be co-hydrolyzed and condensed or alternately an appropriate 1,3-divinyltetraorganodisiloxane, e.g., symmetrical divinyldimethyldiphenylsiloxane or divinyltetramethylsiloxane, which furnishes the endgroups of the polydiorganosiloxane, may be equilibrated with an appropriate dipolyorganosiloxane, e.g., octamethylcyclotetrasiloxane, in the presence of an acidic or basic catalyst. Regardless of the method of preparation of polydiorganosiloxane (A), there is usually coproduced a varying quantity of volatile, cyclic polydiorganosiloxanes.

The viscosities of the polydiorganosiloxanes (A) defined above for the purposes of this invention, refer preferably essentially free of cyclic polydiorganosiloxanes (less than 1 wt.%, preferably 0.5 wt.% measured for 1 h 150 °C 20 mbar) portion of the polyorganosiloxane. This essentially cyclic free portion can be prepared by stripping the polydiorganosiloxane at 150 °C for at least 1 hours to yield a polymer residue of this type. This residue will be essentially free of cyclic material with the exception of trace quantities of macrocyclic polydiorganosiloxanes (molweight > 518 g/mol) which are non-volatile as defined above.

The average polymerization degree P_n of the polymer (A) measured by GPC measurement versus polystyrene standard based on the average number mol weight M_n is preferably in the range of > 10 to 12000, the more preferred range is 40 to 6000. The viscosities of such polymers are in the range of 10 to 50,000,000 mPa.s at 25 °C at a shear rate of D=1 s^{-1} . The value for P_n or the index ´b´ in the above formula (IIIa) is such that the linear polyorganosiloxane (A) has a viscosity at 25 °C, of at least 10 mPa.s. Preferably the range of the viscosity is from about 40 mPa.s to 35,000,000 mPa.s and, most preferably from 100 mPa.s to 25,000,000

mPa.s. Said viscosity corresponds approximately to the values of the average P_n, indicated by ´ b´ or ´b1+b1x´.

The concentration of the functional unsaturated groups are in the range of 50 mol.% to 0.033 mol.% (mol-% of functionalized Si-atoms per total of Si-atoms), i.e. in case of polydimethylsiloxanes about preferably 0.002 to 12 mmol /g, more preferred 0.004 – 3 mmol/g.

Said siloxane units can be combined in any molecular arrangement such as linear, branched, cyclic and combinations thereof, to provide polyorganosiloxanes (A1) and (A2) that are useful as component (A). In a preferred embodiment the hydrosilylation-curable composition is solvent-less (less than 1 wt.-% volatiles).

The composition according to the invention is preferably used to coat a solid substrate, such as paper, fabrics or thermoplastic films with an adhesive-releasing layer or for extruding, calendering or molding shaped formed articles, laminates or for ´Formed-In-Place´- sealing masses.

The alkenyl content of the components (A) can be determined here by way of ^1H NMR – see A.L. Smith (ed.): The Analytical Chemistry of Silicones, J. Wiley & Sons 1991 Vol. 112 pp. 356 et seq. in Chemical Analysis ed. by J.D. Winefordner.

The component (A) can be also selected of the group of silanes such as of the general formulae:

$R_eR^1_fSi(OR^9)_{(4-e-f)}$

$R_eR^1_fSi(NR^9_2)_{(4-e-f)}$

wherein R, R^1 is as defined above, R^9 is as defined below, and

e = 0 - 3

f = 1 – 4, and

e + f = 4;

$(R^9O)_{(3-g-h)}(R^1{}_g)(R_h)$**Si-$R^2$-Si**$(R_h)(R^1{}_g)(OR^9)_{(3-h-g)}$,

$(R^9{}_2N)_{(3-g-h)}(R^1{}_g)(R_h)$**Si-$R^2$-Si**$(R_h)(R^1{}_g)(NR^9{}_2)_{(3-h-g)}$,

wherein R, R^1 and R^2 is as defined above, R^9 is as defined below, and

g = 1-3,
h = 0-2, and
g + h = 3.

Component (B) -Crosslinker

The curable compositions of the invention use a crosslinker and/or chain extender component (B) for the polymers defined under (A). The component (B) is from the group consisting of silanes, siloxanes having at least 2 SiH groups which can react with alkenyl groups of the polymers (A) and crosslink both polymers to an elastomeric network. In order to get a more elastomeric behaviour rather than a gel it is preferred that at least 30 mol.-% of the component (A) or (B) should have a functionality of reactive groups of 3 or more (number of Si-alkenyl groups per total of Si atoms for (A) and number of SiH-groups per total of Si atoms for (B)).

The component (B) is preferably selected from the group of SiH-containing polyorganosiloxanes and SiH-containing organosilanes respectively hydrogen silyl modified hydrocarbons. Suitably component (B) is composed of siloxane units selected from the groups M= $R_3SiO_{1/2}$, M^H=$RYSiO_{1/2}$, D=$R_2SiO_{2/2}$, D^H=$RYSiO_{2/2}$, T=$RSiO_{3/2}$, T^H=$YSiO_{3/2}$, $SiO_{4/2}$, wherein R is as defined above and Y = R^1 and/or H, with the proviso that there are in average at least two SiH-groups per molecule.

For example, they include:

$R_eH_fSi(OR^9)_{(4-e-f)}$

$R_eH_fSi(NR^9{}_2)_{(4-e-f)}$

wherein R is as defined above, R^9 is as defined below, and

e = 0 – 3

f = 1 – 4, and

e + f = 4.

Further

$(R^9O)_{(3-g-h)}(H_g)(R_h)$**Si-$R^2$-Si**$(R_h)(H_g)(OR^9)_{(3-h-g)}$,

$(R^9{}_2N)_{(3-g-h)}(H_g)(R_h)$**Si-$R^2$-Si**$(R_h)(H_g)(NR^9{}_2)_{(3-h-g)}$,

wherein g, h, R, R^2, R^9 is as defined above or below.

This means the polymer (B) can be formally described by the ratios of the general formula (II),

$$[M_{a2}D_{b2}T_{c2}Q_{d2}]_{m2} \qquad (IV)$$

wherein the siloxy units M, D, T and Q are as defined above including the possible SiH-containing M, D, and T groups. Also possible is that part of the siloxy groups are alkenyl siloxy groups, as long as there are at least in average two SiH-groups per molecule. The siloxy units can be distributed blockwise or randomly in the polymer chain. Within a polysiloxane chain each siloxane unit can be identical or different and preferably

a2 = 1-10

b2 = 0-1000

c2 = 0-50

d2 = 0-1

m = 1-2000

The afore mentioned indices should represent the average polymerisation degree P_n based on the average number molecular mass M_n.

The range for M-, D- ,T- and Q-units present in the molecule can cover nearly all values representing fluids, flowable polymer, liquid and solid resins. It is preferred to use liquid silanes or liquid linear, cyclic or branched siloxanes comprising optionally remaining C_1-C_3-alkoxy or Si-hydroxy groups remaining from the synthesis. These compounds can have a low molecular weight or are condensation products, which can be partially hydrolyzed, as well as siloxanes polymerized via an equilibration or a condensation reaction under the assistance of acidic catalysts.

The siloxane units with radicals R or Y can be equal or different for each silicon atom.

The preferred structures of reactive polyorganosiloxanes for component (B) in the compositions of this invention are silanes or condensed silanes/siloxanes of formula (IVa) to (IVd).

The preferred structure composed with these units are selected from

$$Y_r\,R_{3-r}SiO(R_2SiO)_z(RYSiO)_vSiR_{3-r}Y_r \qquad \text{(IVa)}$$

$$Y_rMe_{3-r}\,SiO(Me_2SiO)_z(MeYSiO)_vSiMe_{3-r}\,Y_r \qquad \text{(IVb)}$$

$$Me_3SiO(MeYSiO)_vSiMe_3 \qquad \text{(IVc)}$$

$$[YRSiO]_w \qquad \text{(IVd)}$$

z = 0 to 1000

v = 0 to 100

z+v = 1 to 1000

w= 3 to 9

r= 0 or 1,

and structures of the formula

$$\{[YSiO_{3/2}][R^9O_{1/2}]_{n2}\}_{m2} \quad \text{(IVe)}$$

$$\{[SiO_{4/2}\}][R^9O_{1/2}]_{n2}[R_2YSiO_{1/2}]_{0,01\text{-}10}[YSiO_{3/2}]_{0\text{-}50}[RYSiO_{2/2}]_{0\text{-}1000}\}_{m2} \quad \text{(IVf)}$$

wherein $R^9O_{1/2}$ is an alkoxy residue at the silicon atom

n2= 0.001 to 3
a2 = 0.01- 10
b2 = 0-1000
c2 = 0- 50
m2 = 1 to 2000

Y= hydrogen or R^1

R^9 is hydrogen, n-, iso-, tertiary- or cyclo- C_1-C_{25}-alkyl, such as methyl, ethyl, propyl, alkanoyl, such acyl, aryl, -N=CHR, such as butanonoxime, alkenyl, such as propenyl, which groups R^9 may be substituted by one or more halogen atoms, pseudohalogen groups, like cyano.

The preferred groups for Y are hydrogen.

One preferred embodiment of the compounds of class (IVe) and (IVf) is provided by way of example by monomeric to polymeric compounds which can be described via the formula $[(Me_2HSiO_{0.5})_kSiO_{4/2}]_{m2}$ wherein index k can have integer or decimal values from 0.01 to $(2*m_2+2)$. Such liquid or resinous molecules can contain significant concentrations of SiOH- and/or (C_1-C_6)-alkoxy-Si groups up to 10 mol.% related to the silicon atoms.

The indices z and v for the other types of preferred compounds with the formulas (IVa) to (IVc) are in the range of 0-1000 defined as average P_n based on the number average mol mass M_n measured by GPC versus a polystyrene standard.

Other examples of preferred suitable compounds for component (B) in the compositions of this invention include $HMe_2SiO(Me_2SiO)_zSiMe_2H$, $Me_3SiO-(MeHSiO)_v-SiMe_3$, $(MeHSiO)_{3-6}$, $Si(OSiMe_2H)_4$, $MeSi(OSiMe_2H)_3$. $HMe_2SiO-(Me_2SiO)_{z1}(MePhSiO)_{z2}(MeHSiO)_vSiMe_2H$, wherein z1+z2 = z.

The component (B) can be used as a single component of one polyorganosiloxane polymer or mixtures thereof. In preferred alternative mixtures of formula (IVb) and (IVc) are used. If the increase of the cure rate is required, it is preferred to use some organopolysiloxanes (B) having $HMe_2SiO_{0,5}$-units to adjust the cure rate to shorter times.

The molecular weight of component (B) is smaller, the functionality in (B) per molecule is higher compared to component (A).

If it is necessary to still further increase the cure rate, this can be achieved by way of example via an increase of the molar ratio of SiH to Si-alkenyl, or an increased amount of catalyst (C), or an increase in the proportion of polyorganosiloxanes (B), which contain $HMe_2SiO_{0.5}$ units. Thus preferred components (B) include $HMe_2SiO_{0.5}$ (MH groups), in order to provide faster curing rates.

In a further preferred embodiment, of the component (B) this component is selected from the group according to formula (IVa) which consist of a component (B1) such as $YR_2SiO(R_2SiO)_z(RYSiO)_vSiR_2Y$ or formula (IVc) having a functionality of Y of 3 or more, and a component (B2) having a functionality of Y of 2 in average such as $YR_2SiO(R_2SiO)_zSiR_2Y$, wherein Y, R and z are as defined above.

If (B1) and (B2) are used together, the preferred ratio of functionality SiH (B1) to (B2) is from more than 0 to 70 mol-%, and more preferably from 30 to 100 mol-% of (B2), based on (B1) and (B2).

The molecular weight for the component (B) is not critical; however it is preferred such that the polyorganosiloxane component (B) has a viscosity at 25 °C up from 3 to 10,000 mPa.s in the case of R= methyl. The viscosity depends upon the kind of the R and Y substituents, and the ratio of the units M, D, T and Q as well as the molecular weight.

It is preferred to use liquid siloxanes with a low mol weight, i.e. smaller than 1,000,000 g/mol, preferably smaller than 75,000 g/mol in case of polydimethyl-methylhydrogensiloxanes.

The siloxane units with radicals R or Y can be equal or different for each silicon atom. Each molecule can bear one or more groups independently.

The crosslinker (B) should have at least more than 2 reactive groups Y per molecule whereas the chain extender (B2) have a functionality Y of 2 to 3 in average per molecule.

The concentration of the reactive group Y is in the range of 0.2 to 100 mol.% Y groups related to Si atoms, i.e. for polydimethyl–methylhydrogensiloxane preferably about 0.1 –17 mole SiY/g, the preferred range is 0.15 to 16 mole/g.

In one preferred embodiment a mixture of compounds having formula (IVc) or (IVd) are used together with (IVa) and/or (IVb), where z= 0, R= methyl and the SiH concentration is preferably >7-17 mmol SiH/g and in the second compound of (B) the index z > 0 wherein the SiH concentration has values of preferably 0.2 to 7 mmol SiH/g.

It is preferred to use compounds of formula (IVa) and/or (IVb) wherein R= aryl in particular phenyl, if adherence onto other substrates such as thermoplastic substrates has to be achieved.

The SiH-content in the present invention is determined by way of ^{1}H-NMR, see A.L. Smith (ed.): The Analytical Chemistry of Silicones, J. Wiley & Sons 1991 Vol. 112 pp. 356 et seq. in Chemical Analysis ed. by J.D. Winefordner.

The ratio of the crosslinker (B) to polymer (A) necessary for getting an elastomeric network, i.e. a non-sticky surface can be calculated by the ratio of reactive groups in (B) and (A). It is preferred to have an excess of reactive groups (B) : (A) of 0.7 to 20 : 1, preferably 1.2 to 6 : 1, more preferably 1.5 to 4 : 1 in order to ensure a certain level of multifunctional structures in the cured elastomeric network.

Component (C) - catalyst

The inventive composition contains at least one hydrosilylation catalyst as component (C) selected from the group of organo metal compounds, salts or metals, wherein the metal is selected from the group of Ni, Ir, Rh, Ru, Os, Pd and Pt compounds as taught in US 3,159,601; US 3,159,662; US 3,419,593; US 3,715,334; US 3,775,452 and US 3,814,730.

The component (C) for the hydrosilylation reaction of the inventive composition is a catalyst compound, which facilitates the reaction of the silicon-bonded hydrogen atoms of component (B) with the silicon-bonded olefinic hydrocarbon substituents of component (A). The metal or organo metal compound can be any platinum group metal-containing a catalytic active component. The catalyst (C) includes complexes with sigma- and pi-bonded carbon ligands as well as ligands with S-,N, or P atoms, metal colloids or salts of the afore mentioned metals. The catalyst can be present on a carrier such as silica gel or powdered charcoal, bearing the metal, or a compound or complex of that metal. Preferably, the metal of component (C) is any platinum complex compound.

Typical the platinum containing catalyst component in the polyorganosiloxane compositions of this invention is any form of platinum (0), (II) or (IV) compounds which are able to form complexes with the inventive phosphites. Preferred complexes are Pt-$^{(0)}$-alkenyl complexes, such alkenyl, cycloalkenyl, alkenylsiloxane such vinylsiloxane, because of its easy dispersibility in polyorganosiloxane systems. A particularly useful form of the platinum complexes are the $Pt^{(0)}$-complexes with aliphatically unsaturated organosilicon compound such as 1,3-divinyltetramethyl-disiloxane (Vinyl-M2 or Karstedt catalyst), as disclosed by US 3,419,593 incor-

porated herein by reference are expecially preferred, cyclohexen-Pt, cyclooctadien-Pt and tetravinyltetramethyl-tetracyclosiloxane (Vinyl-D4).

Pt^0-olefin complexes are prepared by way of example in the presence of 1,3-divinyl-tetramethyldisiloxane (M^{Vi}_2) via reduction of hexachloroplatinic acid or of other platinum chlorides by the way of example by alcohols in the presence of basic compounds such as alkali carbonates or hydroxides.

The amount of platinum-containing catalyst component that is used in the compositions of this invention is not narrowly limited as long as there is a sufficient amount to accelerate the hydrosilylation between (A) and (B) at the desired temperature in the required time (B) in the presence of all other ingredients of the inventive composition. The exact necessary amount of said catalyst component will depend upon the particular catalyst, the amount of other inhibiting compounds and the SiH to olefin ratio and is not easily predictable. However, for platinum catalysts said amount can be as low as possible due to cost reasons. Preferably one should add more than one part by weight of platinum for every one million parts by weight of the organosilicone components (A) and (B) to ensure curing in the presence of other undefined inhibiting traces. For the compositions of this invention, which are to be used by the coating method of this invention the amount of platinum containing catalyst component to be applied is preferably sufficient to provide from 1 to 200 ppm preferably 2 to 100 ppm, especially preferred 4 to 60 ppm by weight platinum per weight of polyorganosiloxane components (A) plus (B).

Preferably said amount is at least 4 ppm by weight per sum of (A) and (B).

The hydrosilylation catalyst can also be selected from the group of photoactivatable catalysts.

These catalysts capable of being photoactivated preferably contain at least one metal selected from the group composed of Pt, Pd, Rh, Co, Ni, Ir or Ru. The photoactivatable catalyst preferably comprises platinum.

Photoactivatable catalysts are preferably selected among organometallic compounds, i.e., comprise carbon-containing ligands, or salts thereof. In a preferred embodiment photoactivatable catalyst (C) has metal carbon bonds, including sigma- and pi-bonds. Preferably the photoactivatable catalyst (C) is an organometallic complex compound having at least one metal carbon sigma bond, still more preferably a platinum complex compound having preferably one or more sigma-bonded alkyl and/or aryl group, preferably alkyl group(s). Sigma-bonded ligands include in particular, sigma-bonded organic groups, preferably sigma-bonded C_1-C_6-alkyl, more preferably sigma-bonded methyl groups, sigma-bonded aryl groups, like phenyl, sigma-bonded silyl groups, like trialkyl silyl groups. Most preferred photoactivatable catalyst includes η^5-(optionally substituted)-cyclopentadienyl platinum complex compounds having sigma-bonded ligands, preferably sigma-bonded alkyl ligands.

Further photoactivatable catalysts include (η-diolefin)-(sigma-aryl)-platinum complexes (see e.g. US 4,530,879).

The photoactivatable catalyst can be used as such or supported on a carrier.

The photoactivatable catalyst is a catalyst, which provides additional options to extend the bath-life time of the reactive silicon based composition in addition to the inventive phosphites and allows enlarging the processing time prior to gelling of the components.

Examples of photoactivatable catalysts include η-diolefin-σ-aryl-platinum complexes, such as disclosed in US 4,530,879, EP 122008, EP 146307 (corresponding to US 4,510,094 and the prior art documents cited therein), or US 2003/0199603, and also platinum compounds whose reactivity can be controlled by way for example using azodicarboxylic esters, as disclosed in US 4,640,939 or diketonates.

Photoactivatable platinum compounds that can be used are moreover those selected from the group having ligands selected from diketones, e.g. benzoyl-

acetones or acetylenedicarboxylic esters, and platinum catalysts embedded into photo-degradable organic resins. Other Pt catalysts are mentioned by way of example in US 3,715,334 or US 3,419,593, EP 1 672 031 A1 and Lewis, Colborn, Grade, Bryant, Sumpter, and Scott in Organometallics, 1995, 14, 2202-2213, all incorporated by reference here.

Photoactivatable catalysts can also be formed in-situ in the silicone composition to be shaped, by using Pt^0-olefin complexes and adding appropriate photo-activatable ligands thereto.

The photoactivatable catalysts that can be used here are, however, not restricted to these above-mentioned examples.

The most preferred photoactivatable catalysts to be used in the process of the invention are (η^5-cyclopentadienyl)-trimethyl-platinum, (η^5-cyclopentadienyl)-triphenyl-platinum complexes, in particular, (η^5-methylcyclopentadienyl)-trimethyl-platinum.

The component (C) can also be selected from the group of reaction products of the platinum group metal-containing catalysts (C) and component (D) whereby each of the component is defined under (C) and (D).

The amount of the photoactivatable catalysts is preferably 1-500 ppm and preferably in the same lower range as defined for the heat-activatable hydrosilylation catalysts mentioned above.

As explained already above, the specific phosphites used in accordance with the invention interact with those conventional transition metal compounds through ligand exchange reactions, thereby influencing the hydrosilylation activity of the catalyst to provide surprisingly an excellent balance between storage stability on the one hand and reactivity at elevated temperatures upon curing.

Component (D)

The inhibitor (D) is applied in a sufficient amount in order to further retard the hydrosilylation reaction at room temperature in order to enable mixing of the components (A) to (C) as well as the dispensing and coating step without prior curing.

On the other hand the cure rate after coating should be achieved in the shortest possible time after heat or light activation within seconds especially above 40 °C.

With respect to the component (D) it can be referred to the phosphites having the formula:

$$P(OR)_3 \qquad (I)$$

as defined above.

Inhibitor compound (D) may be preferably incorporated therein in small amounts, such as less than 2 wt.% (20000 ppm) based on the total weight of (A) to (B).

A particularly preferred range is 0.2 to 12000 ppm of component (D) related to (A) and (B).

Furthermore preferably the molar ratio of the transition metal derived from component (C) platinum to the phosphite (D) is from 1:1 to 1:6.

Due to their interaction with the transition metal hydrosilylation catalyst compound, the component (D) act as an inhibitor on the hydrosilylation reaction thereby increasing storage stability, and at the same do not exert their inhibiting activity during curing reaction.

As the case may be, it might be desirable to add additionally other conventional inhibitors, that is, to combine the inventive phosphites of component (D) with other conventional inhibitors in order to further modulate the hydrosilylation activity. In this case the preferred amounts for the component (D) included the amount of the other conventional inhibitors.

Thus, the inventive compositions may contain an appropriate amount of one or more additional conventional inhibitors. Preferably, however, the inventive compositions do not contain other phosphorous inhibitor compounds than those of formula (I).

Conventional inhibitors for the platinum group metal catalysts are well known in the organosilicon art. Examples of various classes of such metal catalyst inhibitors include unsaturated organic compounds such as ethylenically or aromatically unsaturated amides, US 4,337,332; acetylenic compounds, US 3,445,420 and US 4,347,346; ethylenically unsaturated isocyanates, US 3,882,083; olefinic siloxanes, US 3,989,667; unsaturated hydrocarbon diesters, US 4,256,870, US 4,476,166 and US 4,562,096, and conjugated eneynes. US 4,465,818 and US 4,472,563; other organic compounds such as hydroperoxides, US 4,061,609; ketones, US 3,418,731; sulfoxides, amines, nitriles, US. 3,344,111; diaziridines, US 4,043,977; and various salts, such as US 3,461,185, phosphorous compounds preferably excluded. Examples thereof include the acetylenic alcohols of US 3,445,420, such as ethynylcyclohexanol and methylbutynol; the unsaturated carboxylic esters of US 4,256,870, such as diallylmaleate and dimethyl maleate; and the maleates and fumarates of US 4,562,096 and US 4,774.111, such as diethyl fumarate, diallyl fumarate and bis-(methoxyisopropyl)maleate. The half esters and amides of US 4,533,575; and the inhibitor mixtures of US 4,476,166 would also be expected to behave similarly.

The above-mentioned patents relating to conventional inhibitors for platinum group metal-containing catalysts are incorporated herein by reference.

Component (E)

The siloxane composition according to the invention may comprise further ingredients (E) as auxiliary additives. The siloxane compositions according to the invention may also comprise further ingredients, by way of example solvents (E), fillers, pigments or process aids added to achieve better process properties for the inventive polymer composition (A) to (D).

If the compositions of the present invention optionally comprise solvents these solvents are usual organic solvents in the range of less than 20 wt.-% , preferably less than 10 wt.-% and most less than 5 wt.-% related to (A) to (D). Appropriate reactive solvents can be selected from the group of olefinic hydrocarbons such as alpha-olefins, e.g. C_8-C_{25}-alpha-olefins, preferably C_{14}-C_{20}-alpha-olefins or evaporable siloxanes having moleweight below 518 g/mol without alkenyl or SiH groups. Mixtures of alpha-olefins can also be used.

Other additives falling under definition of component (E) are selected from the group of heat stabilizers, coloring compounds or pigments, antioxidants, biocides, fungicides, such as Preventol®, Katon®, Dowicil®, fillers, espec. spherical silsesquioxanes for getting additional antiblocking properties of release layers, anti-mist additives as disclosed in US 6,586,535 or US 2003/0134043, anchorage additives, slipping agents as disclosed in EP 819735 A1 and further auxiliary components typical for silicone release compositions. These other ingredients may be contained in said reactive silicon-based composition in a total amount of up to 20 wt.%.

If fillers are used in inventive compositions the amount of filler is between 1 to 300 weight parts, preferably 15 to 80 weight parts related to 100 weight parts of component (A). The fillers are preferably selected from the groups of hydrophilic or hydrophobic, preferably surface-modified fillers. The fillers may serve as reinforcing fillers, thickening additive, as anti-blocking or anti-friction or matting additive.

The fillers include by way of example are all of the fine-particle fillers, i.e. those having particles smaller than 100 µm (sieve residue), i.e. preferably composed of particles smaller than this value. These can be mineral fillers, such as silicates, carbonates, nitrides, oxides, carbon blacks, or silicas being fumed or precipitated silica, whose BET-surface areas are from 0.3 to 400 m^2/g, these preferably having been specifically surface-hydrophobized here. Preferred silicas are, for example, Aerosil® 200, 300, HDK® N20 or T30, Cab-O-Sil® MS 7 or HS 5 more than 200 m^2/g BET surface area or precipitated silicas, or wet silicas, are Vulkasil®VN3, or FK 160 from Degussa, or Nipsil®LP from Nippon Silica K.K. and others. Examples of commercially available silicas pre-hydrophobized with various silanes are: Aerosil® R 972, R 974, R 976, or R 812, or, for example, HDK® 2000 or HDK® H30, names for materials known as hydrophobized precipitated silicas or wet silicas are Sipernat®D10 or D15 from Degussa.

Surfaced treated fillers having low BET-values are preferred because the ability to build up shear thinning effects is reduced. The preferred surface treatment can be achieved with polyorganosiloxanediols, polyorganosiloxanes, alkoxy- or chloro-silanes, which allows a certain concentration of fillers having lowest degree of thickening properties and shear thinning.

Another class of fillers serving as non-transparent non-reinforcing fillers are powdered quartz, diatomaceous earths, powdered crystobalites, micas, aluminum oxides, aluminum hydroxides, oxides and salts of Fe, Mn, Ti, Zn, Zr, chalks, or carbon blacks, whose BET-surface areas are from 0.3 to 50 m^2/g.

These fillers are available under variety of trade names, examples being Sicron®, Min-U-Sil®, Dicalite®, Crystallite® and serve as matting agents. Such fillers are used if present in a concentration of about 1 to 300 weight parts, preferably 5 to 100 weight parts related to 100 weight parts of (A).

Some very special fillers can used as matting agent, agent for increasing the mechanical modulus, or anti-blocking agent, these filler are selected from the group of spherical or fiber shaped thermoplastic powders or fibers such as PTFE-powders, PTFE-emulsions or polyamide, polyurethane or silsesquioxanes powders,

thermoplastic fibers cured silicone elastomers or resins und are used if present in amounts of up to 10 weight parts related to 100 weight parts of (A). Tradenames are Teflon® emulsions, Nylon®-powders, Tospearl®, Acemat® , Twaron®, Kevlar®, Dralon®, Diolen® etc.

This type of filler especially if the particles have a spherical shape can preferably be used as anti-blocking agents in the release layer and can give an especially soft touch and low friction properties of the rubber surfaces.

Another class of additives are stabilizers, such as heat stabilizers which can be selected from the group of metal compounds, organic or inorganic salts, complexes of Ce, Fe, La, Mn, Ti and Zr.

Levelling agents, mold release agents are selected from the group consisting of polyether-siloxanes, polyols, polyethers, polyhalides, fatty alcohol or fluoroalkyl derivatives.

Another class of important auxiliary additives are adhesion promotors, which can either be incorporated in the composition (A) to (D) or applied in an appropriate form as primer applied prior onto the substrate foreseen for getting adhered to the rubber composition under curing.

Adhesion promotors are selected from the group of preferably alkoxysilanes, their condensation product alkoxysiloxanes bearing further organofunctional groups linked over Si-C-bonds, in particular epoxyalkyl, acryloxyalkyl, methacryloxyalkyl, NCO-alkyl, aminoalkyl, urethanealkyl, alkenyl, which further can bear SiH groups. Such silanes/siloxanes can be combined with condensation catalyst selected from the group of organometal compounds of Ca, Zr, Zn, Sn, Al or Ti and /or polycyclic aromatic compounds having reactive groups such as alkenyl substituted aromatic biphenyl ethers, esters. The effects of adhesion can be further improved by the addition of selected compounds of component (B), e.g. incorporated by reference US 4,082,726, US 5,438,094; US 5,405,896; US 5,536,803; US 5,877,256; US 6,602,551; EP 581504 A and EP 875536.

The present invention further relates to novel phosphites having the formula:

$P(OR)_3$ (I)

wherein R is an organic group, and at least one group R is an aliphatic group comprising at least one substituted or unsubstituted polycycloaliphatic group, with the exception of tris{bicyclo[2.2.1]hept-2-yl} phosphite and tris{adamantan-1-yl} phosphite, and the use of one or more phosphites of the formula (I) for the manufacture of hydrosilylation-curing polyorganosiloxane and/or silane compositions. Further the present invention relates to the use of one or more phosphites of formula (I) as inhibitors of the hydrosilylation reaction in the curing of polyorganosiloxane compositions and/or silane compositions.

In another preferred embodiment the present invention relates to hydrosilylation-curing polyorganosiloxane compositions and/or silane compositions comprising:

100 parts per weight (pw) of component (A) as defined above,
0.1 – 200 pw of component (B) as defined above,
0.1 – 1000 ppm of the transition metal contained in component (C) related to (A) and (B) each as defined above,
0.2 to 12000 ppm of component (D) related to (A) and (B), each as defined above, and
0 to 200 pw of component (E) as defined above.

In the hydrosilylation-curing polyorganosiloxane compositions and/or silane compositions according to the invention preferably the molar ratio of platinum to phosphite of formula (I) is from 1:1 to 1:6.

In another preferred embodiment the present invention relates to a so-called one-part hydrosilylation-curing polyorganosiloxane and/or silane composition, comprising at least one or more phosphites of formula (I).

Under the expression ´One-Part´- hydrosilylation-curing polyorganosiloxane and/or silane compositions it is meant in accordance with the present invention, that composition (A) to (D) and optionally (E) comprises all ingredients to get cured under the appropriate conditions, in particular at an increased temperature level of higher than 25 °C.

The present invention further relates to cured polyorganosiloxane and/or silane compositions obtained by curing the hydrosilylation-curing polyorganosiloxane and/or silane compositions as defined above.

Further the present invention relates to the use of the hydrosilylation-curing polyorganosiloxane compositions and/or silane compositions of the invention for the manufacture of shaped formed articles, extruded articles, coatings, and sealants.

In particular, in the manufacture of shaped articles formed under extrusion there is an increasing demand for curing such rubber articles via a hydrosilylation reaction while replacing peroxides. The cure rates necessary for such technology are rather high i.e. the cure time is short at higher temperatures, and is in general below 2 min at 110 °C in order to get a bubble free cured elastomeric article. These requirements can be achieved with the hydrosilylation-curing polyorganosiloxane and/or silane compositions according to the invention. At the same time the hydrosilylation-curing polyorganosiloxane and/or silane compositions according to the invention have a storage stability at 25 °C of preferably more than 30 days.

The term storage stability used in accordance with the present invention means the t_{10} time at 25 °C, which is the time wherein 10 % of the elastic modulus of the fully cured material at 25 °C is reached, after preparation of the reactive composition. On the other hand the cure time of the hydrosilylation-curing polyorganosiloxane and/or silane compositions is the time t_{90} at 110 °C, which is the time wherein 90 % of the elastic modulus of the fully cured material at 100 °C is reached after preparation of

the reactive composition. The elastic modulus is measured with a Rheometer MDR 2000 of Alpha Technologies.

Another important application of the hydrosilylation-curing polyorganosiloxane and/or silane compositions according to the invention are siloxane coatings e.g. release coatings for thermoplastic films which must be cured below 110 °C within a reasonable short curing time given by the band speed of the coating machines which is usually between 50 – 1000 m/min whereby the coating thickness is usually between 0.05 – 1 mm.

The present invention further provides a process for the manufacture of the hydrosilylation-curing polyorganosiloxane, comprising mixing one or more

(A) polyorganosiloxanes and/or silanes having in average at least two alkenyl groups,
(B) one or more polyorganosiloxanes and/or silanes having in average at least two SiH groups,
(C) one or more transition metal compounds, wherein the transition metal is selected from group consisting of nickel, ruthenium, rhodium, palladium, osmium, iridium,and platinum,
(D) one or more phosphites as defined above, and
(E) optionally one or more auxiliary agents,
in a mixing apparatus.

Preferably the following procedure is applied to prepare the preferred 'One-Part'-composition of the invention.

That is, the components (A) to (E) are mixed first to non-reactive compositions, that is, compositions, which do not contain (A), (B) and (C) at the same time.

Although the ´One-Part'-composition of the invention has a very high stability, i.e. a very long storage time, it is nevertheless in practice preferred to prepare and supply two or three partial compositions, wherein each partial composition does not contain all of the components (A) to (E). Those partial compositions can be stored practically for more than 100 days. The manufacturer usually prepares the reactive composition i.e. mixing of the partial compositions. The reactive composition has still a storage stability of more than 30 days.

Those preferred partial compositions are most preferably two partial compositions containing the following components:

- (A) + (B) + (D) + optionally (E), e.g. fillers;
- (A) + (C) + optionally (E), e.g. fillers.

Such a combination of the partial compositions is preferred because a 1:1 mixture per volume is achievable, which easily to be mixed by static mixers. Another advantage of such a combination of partial compositions is the avoidance of the simultaneous presence of (B) and (C) which detrimental because of a possible occurrence of discolouration. On the other hand the combination of (A) and (C) has a stabilizing effect on the transition metal catalyst component (C).

The partial compositions as defined before are preferably prepared for example with in a mixing apparatus selected from kneaders, dissolvers, single or twin screw extruders, LIST-mixing apparatuses, BUSS-co-kneader, Banbury mixers or ´press-mixers´ of Voith, two roll-mixers.

The reactive preferably ´One-Part´-compositions are preferably prepared by mixing the partial compositions by mixing the with them for example in a mixing apparatus selected from static mixers, kneaders, like two blade kneaders, dissolvers, single or twin screw extruders, LIST-mixing apparatuses, BUSS-co-kneader, Banbury mixers or ´press-mixers´ of Voith, two roll-mixers, multi roll coating mixtures.

Accordingly the present invention also relates to the partial composition comprising components (A) + (B) + (D) + optionally (E).

Preferred compositions:

The inventive compositions preferably applied as ´One-Part´-composition can be used preferably as a so-called paper release coating, as a liquid rubber or as a high consistency rubber composition having optionally incorporated reinforcing fillers, which for example have the following compositions:

(A) 100 parts per weight (pw) of one or more polyorganosiloxanes and/or silanes having in average at least two alkenyl groups and a viscosity of 50 mPa.s – 100 kPa.s at 25 °C,

(B) 0.1 to 100 pw of one or more polyorganosiloxanes and/or silanes having in average at least two SiH groups in an amount to achieve a molar ratio of SiH : Si-alkenyl groups of 0.8 to 6 : 1,

(C) 1- 500 ppm calculated as metal related to (A) and (B) of one or more transition metal compounds, wherein the transition metal is selected from group consisting of nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum,

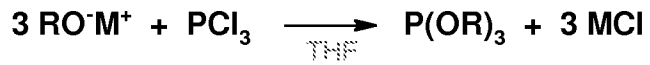
(D) one or more phosphites according to formula (I) preferably in an amount to achieve a molar ratio of 1:1 to 6:1 of component (D) to the metal atom of component (C), and

(E) 0 – 200 pw of one or more reinforcing silicas having a BET–surface of more than 50 m^2/g and optionally further auxiliary additives.

EXAMPLES

Synthesis of the phosphite inhibitors

The triorganophosphites (1-5) have been synthesized according to the following reaction scheme



R= cycloalkyl, bicyloalkyl, tricycloalkyl

M= Li, Na

wherein PCl_3 and the corresponding metal alkoxide obtained from a reaction of an alcohol with sodium hydride or n-butyl lithium undergo a reaction in dried tetrahydrofurane, see also A. Earnshaw, N. Greenwood (1997): The Chemistry of the Elements – Second Edition.

General procedure for the synthesis

A solution of the selected alcohol in tetrahydrofurane (THF), which has been dried over sodium and sodium hydride, was added dropwise under vigorously stirring under a dry argon atmosphere to a suspension of NaH dissolved in THF or n-butyl lithium dissolved in hexane at room temperature (25 °C). After the indicated period of stirring and cooling to room temperature the solvent was removed under reduced pressure to dryness, then hexane was added and the suspension containing the organic phase, some hexane and salts are separated by filtration using a canula system. The filtered organic phase was concentrated under reduced pressure followed by crystallization step, wherein the residue has been placed in a freezer at –15 °C for crystallization. The solid product was purified by decantation at –78 °C and dried under vacuum (20 mbar).

Example 1: Synthesis of tricyclohexylphosphite (1)

This phosphite compound was prepared starting from 10 g (100 mmol) of cyclohexanol, 3.66 g of NaH (140 mmol) and 3.84 g (28 mmol) of PCl_3. The reaction of cyclohexanol with NaH was carried out for 24 h at 50 °C. After addition of PCl_3 the mixture was stirred for another 12 h at 65 °C and the product was isolated at room temperature (25 °C) afterwards. Yield 8.28 g (90 %).

The corresponding nuclear magnetic spectras show the characteristic signals:

^{1}H-NMR (300 MHz, C_6D_6, 300 °K) δ(ppm) = 4.27(m, 3H, -OCH); 1.92 (m), 1.64 (m), 1.19 (m) (30H, Cy);

^{13}C-NMR (75.42 MHz, C_6D_6, 300 °K) δ(ppm) = 71.21 (d, -OCH-), 35.05 (d), 25.88, 24.18 (Cy);

^{31}P-NMR (121.47 MHz, C_6D_6, 300 °K) δ(ppm) = 138.85.

Example 2: Synthesis of tris (± 2-norbornylmethyl)phosphite (2)

This phosphite compound was prepared starting from 4.67 g (37 mmol) of ± norbornane-2-methanol, 23.75 ml (38 mmol) of 1.6 mol/L solution of n-butyl lithium in hexane and 1.62 g (11.8 mmol) of PCl_3. After addition of PCl_3 the mixture was stirred for 24 h at room temperature. Yield 4.41 g (92 %). The corresponding spectras show the characteristic signals:

^{1}H NMR (300 MHz, C_6D_6, 300 °K) δ(ppm) = 3.98, 3.85, 3.71 (m, 6H, -OCH_2-); 2.40(bs), 2.33(bs), 2.26(bs), 2.08(bs), 2.07(m), 1.90-0.90(m), 0.65-0.54(m) (norbornyl)

^{31}P NMR (121.47 MHz, C_6D_6, 300 °K) δ(ppm) = 139.14, 139.10, 139.06 (endo and exo isomers).

Example 3: Synthesis of tris-(1-adamantylmethyl)phosphite (3)

This compound was prepared starting from 5 g (30 mmol) of 1-adamantane-methanol, 19.7 ml (31.6 mmol) of 1.6 mol/L solution of n-butyl lithium in hexane and 1.24 g (9.02 mmol) of PCl_3. After addition of PCl_3 the mixture was stirred for 24 h at room temperature. Yield 4.28 g (90 %). The corresponding spectras show the characteristic signals:

^{1}H NMR (300 MHz, C_6D_6, 300 °K) δ(ppm) = 3.60 (d, 6H, -OC*H*$_2$-, J_{H-P} = 6.96 Hz); 1.95 (bs); 1.65 (d) (45H, -C*H*$_2$-, *H*C$(CH_2)_3$),

^{13}C NMR (75.42 MHz, C_6D_6, 300 °K) δ(ppm) = 72.65 (-O-*C*H$_2$-, J_{C-P} = 8.77 Hz); 39.74, 39.69, 37.43, 34.46(d), 28.68

^{31}P NMR (121.47 MHz, C_6D_6, 300 °K) δ(ppm) = 140.31.

Example 4: Synthesis of tris(exo-2-norbornyl)phosphite (4)

This compound was prepared analogously as described for **3**, starting from 5 g (44.6 mmol) of 2-norborneol, 28.7 ml (46 mmol) of 1.6 mol/L solution of n-butyl lithium in hexane and 1.92 g (14 mmol) of PCl_3. After addition of PCl_3 the mixture was stirred for 24 h at 50 °C. Yield 4.64 g (91 %). The corresponding spectras show the characteristic signals:

^{1}H NMR (300 MHz, C_6D_6, 300 °K) δ(ppm) = 4.24, 3.85 (m, 3H, -OC*H*=); 2.44 (bs, 3H, H-C≡); 2.12 (bs, 3H, H-C≡); 1.83(d), 1.75-1.5(m), 1.45-1.2(m), 1.06(d), 0.94-0.83(m)

^{13}C NMR (75.42 MHz, C_6D_6, 300 °K) δ(ppm) = 75.53(d) (J_{C-P} = 9.66 Hz), 43.83, 42.011(t), 35.81, 35.24, 28.68, 24.61

^{31}P NMR (121.47 MHz, C_6D_6, 300 °K) δ(ppm) = 137.75, 137.74, 137.73 (endo); 137.02, 136.97, 136.93(exo).

Example 5: Synthesis of tris(1-adamantyl)-phosphite (5)

This compound was prepared starting from 5 g (32.8 mmol) of 1-adamantanol, 21.12 ml (33.8 mmol) of 1.6 mol/L solution of n-butyl lithium in hexane and 1.80 g (13.1 mmol) of PCl_3. After addition of PCl_3 the mixture was stirred for 24 h at 50 °C. Compound was extracted by addition of two portions of benzene (50 ml) at 50 °C, and obtained solid was washed by hexane. Yield 4.76 g (75 %). The corresponding spectras show the characteristic signals:

^{1}H NMR (300 MHz, C_6D_6, 300 °K) δ(ppm) = 2.27 (d, 18H, -OC(CH_2)$_3$); 2.04, 1.55 (m, 27H, -CH_2-, CH(CH_2)$_3$)

^{13}C NMR (75.42 MHz, C_6D_6, 300 °K) δ(ppm) = 75.65 (d, J_{C-P} = 6.44 Hz); 45.87 (d, J_{C-P} = 6.44 Hz), 36.54, 31.36(d)

^{31}P NMR (121.47 MHz, C_6D_6, 300 °K) δ(ppm) = 137.44.

Example 6: Synthesis of tris(2-methylcyclohexyl)phosphite (6)

This compound was prepared analogously as described for **2**, starting from 10 g (87 mmol) of 2-methylcyclohexanol, 2.88 g of NaH (140 mmol) and 4.03 g (29 mmol) of PCl_3. Reaction of 2-methylcyclohexanol with NaH was conduced for 24 h under reflux. After addition of PCl_3 mixture was stirred for 24 h at 65 °C. Product was isolated at room temperature. Yield 9.45 g (88 %).

^{1}H NMR (300 MHz, C_6D_6, 300 K) δ(ppm) = 4.35, 3.78 (m, 3H, -OCH); 2.25, 2.03 (m, 3H, Me-CH)1.8-1.30 (m, 24H, -CH_2-); 1.25-1.10, 1.0-0.82 (m, 9H, -CH_3) (mixture of isomers)

^{13}C NMR (75.42 MHz, C_6D_6, 300 K) δ(ppm) = 82.84 (m), 78.37 (m), 77,94 (m), 73.10 (m) (-OCH-), 40.75, 39.73, 39.66, 39.62, 39.13 (d), 39.08 (d), 36.68, 36.63, 36.29, 35.42 (dd), 34.14 33.97 (d), 33.72 (d), 32.56 (d), 30.02(d), 26.32, 25.79, 25.58, 25.53, 25.46, 24.43, 25.10, 24.92, 21.94, 19.63, 19.33, 19.27, 19.13, 17.68;

^{31}P NMR (121.47 MHz, C_6D_6, 300 K) δ(ppm) = 144.4, 143.98, 143.88, 143.78, 143.58 (resonance lines coming from *cis* and *trans* isomers).

Example 7: Synthesis of tris(2,6-dimethylcyclohexyl)phosphite (7)

a) Synthesis of 2,6-dimethylcyclohexanol

A portion of 3 g ($7.9x10^{-2}$ mol) $NaBH_4$ and 50 ml of ethanol was placed in a three-necked flask (250 ml) equipped with a reflux condenser and a dropping funnel, under argon. Next, a solution of 10 g ($7.9x10^{-2}$ mol) of the ketone $C_6H_8(CH_3)_2(O)$ in 100 ml of C_2H_5OH was added dropwise. The reaction was conducted for 5 hours at room temperature. Next the reaction mixture was poured onto 200 ml of water and 50 ml of ether were added. The organic phase was separated, the aqueous one extracted with ether (2x50 ml), and the combined organic extracts were dried over $MgSO_4$. After solvent evaporation at reduced pressure, pure 2,6-dimethylcyclohexanol (8 g) was obtained with a yield of 80 %.

^{1}H NMR (300 MHz, C_6D_6, 300 K) δ(ppm) = 3.27 (bs), 3.17 (q) (O-CH), 2.52(t), 2.26 (bs), 2.04 (bs), 1.83 (m); 1.80-1.06 (m, -CH_2-); 1.03-0.7 (-Me);

^{13}C NMR (75.42 MHz, C_6D_6, 300 K) δ(ppm) = 81.92, 77.41, 74.68 (O-**C**H); 40.27, 37.83, 34.67, 33.99, 33.77, 31.75, 30.91, 27.77, 26.45, 26.06, 20.39, 19.24, 19.07, 18.37, 14.11.

b) Synthesis of tris(2,6-dimethylcyclohexyl)phosphite

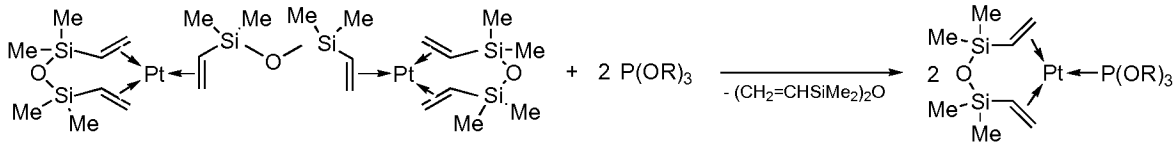
This compound was prepared analogously as described for **3**, starting from 4 g (31 mmol) of 2,6-dimethylcyclohexanol, 28.2 ml (31 mmol) of 1.1 mol/L solution of n-butyllithium in hexane and 1.37 g (10 mmol) of PCl_3. After addition of PCl_3 mixture was stirred for 24 h at room temperature. Yield 3.51 g (85 %).

^{1}H NMR (300 MHz, C_6D_6, 300 K) δ(ppm) = 4.05, 3.88, 3.30 (m, 3H, -OCH-); 2.10-0.83 (m, 42H, -2,6-$(Me)_2$Cy);

^{31}P NMR (121.47 MHz, C_6D_6, 300 K) δ(ppm) = 145.04, 144.94, 143.21, 143.07, 142.97, 142.44, 142.30, 141.53, 140.23 (isomeric phosphites).

Synthesis of transition metal complex compounds

The synthesis follows a pathway in that e.g. the well-known divinyl-tetramethyldisiloxane (´DVTMDS´) bridged binuclear platinum complex (Karstedt's catalyst) can be cleaved by any nucleophile (e.g. phosphite), giving a mononuclear platinum complexes, according to equation:



Example 8: Synthesis of (1,3-Divinyltetramethylsiloxane)[tris(cyclohexyl)-phosphite] platinum (8)

0.15 g (0.457 mmol) of **1**, 4.00 g of Karstedt's catalyst 2.2 wt.% solution in xylene (corresponding to 0.45 mmol Pt) were placed in a Schlenk's flask in argon atmosphere. The reaction was conducted for 24 hours at room temperature under intense stirring with a magnetic stirrer. After this time, the mixture was filtered off by a canula system and the filtrated organic phase was concentrated. The remaining oily residue was washed for three times with pentane and was then separated at – 70 °C by decantation. The precipitate obtained after addition of pentane was dried under vacuum. Yield 0.256 g (80 %).

Example 9: Synthesis of (1,3-Divinyltetramethylsiloxane)[tris(1-adamantyl-methyl)-phosphite] platinum (9)

This compound was prepared analogously as described for **(8)**, starting from 0.29 g (0.550 mmol) of **(3)**, 5.3 ml of Karstedt's catalyst (0.1 M solution in xylene) (0.53 mmol Pt). The obtained complex was dried under vacuum for 24 h. Yield 0.462 g (96 %).

Test conditions for reactivity, i.e cure rate and inhibition (pot-life, storage stability)

The phosphites (1) to (7) were tested in a hydrosilylation reaction, whereby the phosphite was applied as component (D). The alkenyl component (A) is realized by a liquid linear polydimethylsiloxanes having 2 vinyl endgroups, the Si-hydrogen component (B) is realized by a multifunctional polydimethyl-methylhydrogensiloxane (crosslinker), and as component (C) a (platinum)-Karstedt catalyst was choosen.

The testing composition consists of 100 g of component (A), which is a vinyl terminated polydimethylsiloxane with an average chain length of 150 units and a viscosity of 200 to 300 mPa.s (25°C). 1.32 mol.%, 0.177 mmol/g of -CH=CH_2 groups attached to the Si atoms from Momentive Performance Materials.

As second component 7.7 g of the component (B) are admixed, which is a polydimethyl-methylhydrosiloxane, having 1.23 mol.%, of SiH groups represented by the general formula $MD^{H}_{50}D_{110}M$ with 4.42 mmol SiH/g and a viscosity of 35 mPa.s. As third component a solution of 7.8 to 50.1 mg (D) 20-wt.% in toluene providing a molar P : Pt ratio of 1 : 1 to 4: 1 are admixed with a Krups mixer at 25 °C and ambient air. The weights of (A) and (B) provide a molar ratio of in terms of [≡SiH] to [≡Si-CH=CH_2] of 1.93 to 1.

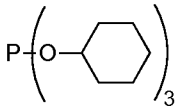
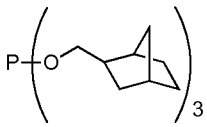
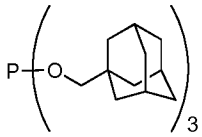
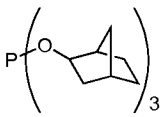
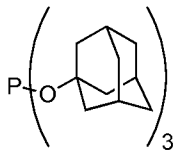
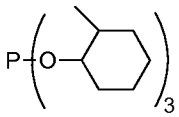
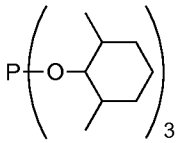
After getting mixed (A),(B) and (D) a solution of the component (C) of 42.2 mg (4.76 10^{-3} mmol) of the Karstedt catalyst solution (2.2 wt.% Pt) in xylene was distributed in the components (A),(B) and (D) corresponding to 10 ppm Pt as metal in total of (A) and (B).

The time for gelling (doubling of viscosity) at 25 °C was measured as pot-life (as measure for storage stability). The relative curing time was measured as the time required until disappearance of 95 % of the initial SiH-signal in the ^{1}H-NMR after storage (A) to (D) at 120 °C. In addition the progress of the reaction has been monitored by DSC-method (Differential Scanning Calorimetry). All samples were mixed well for half an hour in before the DSC analysis. The DSC measurements were made using a DSC 204 NETCH. The instrument was calibrated with indium (ΔH = 28.4 J/g), the heating rate is 10 °K/min running from 20 to 220 °C, hold for 5.0 min at 30 °C under helium atmosphere. The values are average values of 3 runs for each composition.

All the manipulations after mixing were carried out under argon using standard Schlenk and vacuum techniques. ^{1}H-, ^{13}C- and ^{31}P-NMR-spectra were recorded on a Varian Gemini 300 VT and Varian Mercury 300 VT spectrometers in benzene-d6, acetone-d6.

The chemicals were obtained from the following sources: alcohols, benzene-d_6 and acetone-d_6, Karstedt catalyst from Aldrich, Si-vinyl and SiH-siloxanes from Momentive Performance Materials, solvents from POCH Gliwice (Poland).

Table 1

Component (D)	Phosphite	[Pt] : [P]	Pot-life at 25 °C [h]	Curing time at 120 °C [sec]
1 (comparison)		1:1	>168	600
		1:2	>168	900
		1:5	>168	3000
2		1 : 1	5	120
		1 : 2	>168	300
3		1 : 1	2.5	60
		1 : 2	>168	150
4		1 : 1	4	120
		1 : 2	>168	180
5		1 : 1	2	25
		1 : 2	4	75
		1 : 3	>168	140
		1 : 4	>168	510
6 (comparison)		1:1	120	540
		1:2	>168	720
		1:5	>168	1500
7 (comparison)		1:1	72	480
		1:2	>168	780
		1:5	>168	1800

The pot-life times and curing times increase with the increasing ratio of [P] : [Pt], i.e. more phosphite introduced via component (D) increase that time. The reference phosphite (1), (6) and (7) have a pot-life time of more than 72 h (3 days), whereas

the curing time for (1), (6) and (7) is 400 to 3000 sec depending on the molar ratio of [P] : [Pt] of the components (D) to (C).

The addition of tris-(bi- and tricycle)-phosphites such as (2), (3), (4) and (5) into the test composition surprisingly shortens the curing times, whereas the pot-life is still at level of more than 7 days after having prepared the reactive composition. This effect can be used particularly in a kind of ´One-Part´-composition, which is potentially highly reactive on the one hand but can be stored after getting mixed for 7 days on the other hand.

As evidenced by the comparative phosphites (6) and (7) the beneficial effects shown by the inventive polycyclic phosphites is not simply due to an increase in the sterical demand of the phosphites but possibly due to electronic effects not yet understood.

CLAIMS:

1. Hydrosilylation-curing polyorganosiloxane compositions and/or silane compositions, comprising one or more phosphites having the formula:

$$P(OR)_3 \qquad (I)$$

wherein R is an organic group, and at least one group R is an aliphatic group comprising at least one substituted or unsubstituted polycycloaliphatic group.

2. Hydrosilylation-curing polyorganosiloxane compositions and/or silane compositions according to claim 1, comprising:
   (A) one or more polyorganosiloxanes and/or silanes having in average at least two alkenyl groups,
   (B) one or more polyorganosiloxanes and/or silanes having in average at least two SiH groups,
   (C) one or more transition metal compounds, wherein the transition metal is selected from group consisting of nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum,
   (D) one or more of the phosphites as defined in claim 1, and
   (E) optionally one or more auxiliary agents.

3. Compositions according to claim 1 or 2, wherein in the formula (I) all of the groups R are aliphatic groups comprising at least one polycycloaliphatic group.

4. Compositions according to any of claims 1 to 3, wherein the aliphatic group comprising at least one polycycloaliphatic group is a group of the formula:

$$-(CH_2)_x\text{-}A, \qquad (II)$$

wherein x is 0, 1 or 2 and A is a polycycloaliphatic group.

5. Compositions according to any of claims 1 to 4, wherein the polycycloaliphatic group is a saturated or unsaturated group.

6. Compositions according to any of claims 1 to 5, wherein the polycycloaliphatic group is a bi- or tricyclic group.

7. Compositions according to any of claims 1 to 6, wherein the aliphatic group comprising at least one polycycloaliphatic group has from 5 to 30 carbon atoms.

8. Compositions according to any of claims 1 to 7, wherein the polycycloaliphatic group is selected from the group consisting of:

bicyclopentyl,
bicyclohexyl,
bicycloheptyl,
bicyclooctyl,
bicyclononyl,
bicyclodecyl,
tricyclopentyl,
tricyclohexyl,
tricycloheptyl,
tricyclooctyl,
tricyclononyl, and
tricyclodecyl,

which may have 1 to 3 substituents.

9. Compositions according to any of claims 1 to 8, wherein the aliphatic group comprising at least one polycycloaliphatic group is selected from the group consisting of:

bicyclopentylmethyl,
bicyclohexylmethyl,
bicycloheptylmethyl,
bicyclooctylmethyl,
bicyclononylmethyl,
bicyclodecylmethyl,
tricyclopentylmethyl,
tricyclohexylmethyl,
tricycloheptylmethyl,
tricyclooctylmethyl,
tricyclononylmethyl, and
tricyclodecylmethyl,

which may have 1 to 3 substituents.

10. Compositions according to any of claims 1 to 9, wherein the polycycloaliphatic group is selected from the group consisting of:

bicyclo[2.2.1]hept-2-yl,
bicyclo[2.2.1]hept-2-ylmethyl,
adamantan-1-yl,
adamantan-2-yl,
adamantan-1-ylmethyl,
adamantan-2-ylmethyl, and
(+)- and/or (-)-isobornyl.

11. Compositions according to any of claims 1 to 10, selected from the group consisting of:

tris{bicyclo[2.2.1]hept-2-yl} phosphite,
tris{bicyclo[2.2.1]hept-2-ylmethyl} phosphite,
tris{adamantan-1-yl} phosphite,
tris{adamantan-2-yl} phosphite,
tris{adamantan-1-ylmethyl} phosphite,
tris{adamantan-2-ylmethyl} phosphite, and
tris{(+)- and/or (-)-isobornyl} phosphite.

12. Transition metal compound, comprising at least one phosphite having the formula:

$P(OR)_3$ (I),

wherein R is an organic group, and at least one group R is an aliphatic group comprising at least one substituted or unsubstituted polycycloaliphatic group as a ligand, and wherein the transition metal is selected from group of nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum.

13. Transition metal compound, obtained by reacting a transition metal compound, wherein the transition metal is selected from group consisting of nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum, with at least one phosphite as defined in claims 1 to 11.

14. Transition metal compounds according to claims 12 and 13, wherein the transition metal is platinum.

15. Phosphites having the formula:

$P(OR)_3$ (I)

wherein R is an organic group, and at least one group R is an aliphatic group comprising at least one substituted or unsubstituted polycycloaliphatic group, with the exception of tris{bicyclo[2.2.1]hept-2-yl} phosphite and tris{adamantan-1-yl} phosphite.

16. Use of one or more phosphites as defined in any of claims 1 to 10 for the manufacture of hydrosilylation-curing polyorganosiloxane and/or silane compositions.

17. Use of one or more phosphites as defined in any of claims 1 to 10 as inhibitors of the hydrosilylation reaction in the curing of polyorganosiloxane compositions and/or silane compositions.

18. Hydrosilylation-curing polyorganosiloxane compositions and/or silane compositions according to any of claims 1 to claim 11, comprising:

100 pw of component (A),
0.1 – 200 pw of component (B)
0.1 – 1000 ppm of the transition metal contained in component (C) related to (A) and (B),
0.2 to 12000 ppm of component (D) related to (A) and (B),
0 to 200 pw of component (E).

19. Hydrosilylation-curing polyorganosiloxane compositions and/or silane compositions according to any of claims 1 to 11 and 18, wherein the molar ratio of platinum to phosphite is from 1:1 to 1:6.

20. ´One-Part´-hydrosilylation-curing polyorganosiloxane and/or silane compositions, comprising at least one or more phosphites as defined in any of the claims 1 to 11.

21. Cured polyorganosiloxane and/or silane compositions obtained by curing the hydrosilylation-curing polyorganosiloxane and/or silane compositions as defined in any of the claims 1 to 11, and 18 to 20.

22. Use of the hydrosilylation-curing polyorganosiloxane compositions and/or silane compositions of any of claims 1 to 11, and 18 to 21 for the manufacture of shaped formed articles, extruded articles, coatings, and sealants.

23. A process for the manufacture of the hydrosilylation-curing polyorganosiloxane compositions of claims 1 to 11, and 18 to 21, comprising mixing

(A) one or more polyorganosiloxanes and/or silanes having in average at least two alkenyl groups,
(B) one or more polyorganosiloxanes and/or silanes having in average at least two SiH groups,
(C) one or more transition metal compounds, wherein the transition metal is selected from group consisting of nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum,
(D) one or more phosphites as defined in any of the claims 1 to 11, and
(E) optionally one or more auxiliary agents
in a mixing apparatus.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/059513

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L83/04 C08K5/524

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08L C08K

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 078 022 A (CHEN MARK CHAOMING) 7 March 1978 (1978-03-07) example 4	1-11, 16-23
A	US 2006/128881 A1 (GEORGE CATHERINE [FR] ET AL) 15 June 2006 (2006-06-15) claims 1,15-22	1-11, 16-23

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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

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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 January 2009	14/04/2009

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Fax: (+31–70) 340–3016	Buestrich, Ralf

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2008/059513

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers allsearchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search reportcovers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

see Annex

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-11,16-23

Invention 1 (claims 1-11 and 16-23) claims hydrosilylation-curing polyorganosiloxane compositions comprising phosphites according to the formula P(OR)3 wherein R is an organic group, and at least one group R is an aliphatic group comprising at least one substituted or unsubstituted polycycloaliphatic group and a related use and process.

---

2. claims: 12-14

Invention 2 (claims 12-14) claims a transition metal compound, comprising a phosphite according to the formula P(OR)3 wherein R is an organic group, and at least one group R is an aliphatic group comprising at least one substituted or unsubstituted polycycloaliphatic group.

---

3. claim: 15

Invention 3 (claim 15) claims phosphites according to the formula P(OR)3 wherein R is an organic group, and at least one group R is an aliphatic group comprising at least one substituted or unsubstituted polycycloaliphatic group.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2008/059513

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4078022 A	07-03-1978	CA 1089484 A1	11-11-1980
		JP 52156847 A	27-12-1977
		JP 61000835 B	11-01-1986
US 2006128881 A1	15-06-2006	AU 2003294075 A1	29-07-2004
		BR 0316597 A	01-03-2006
		CN 1738867 A	22-02-2006
		EP 1567593 A1	31-08-2005
		FR 2848215 A1	11-06-2004
		WO 2004061003 A1	22-07-2004