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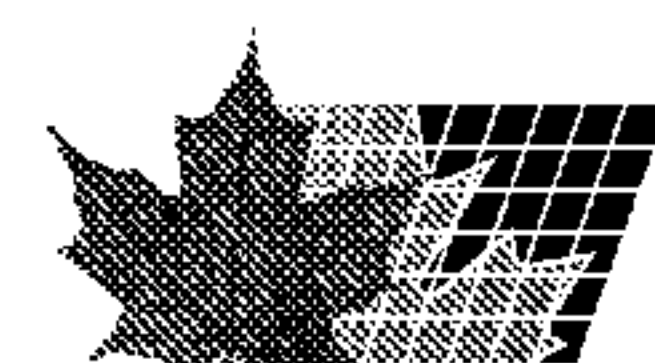
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(54) Title: TWO COMPONENT SILICONE RUBBER WITH IMPROVED COMPRESSION SET PREPARED FROM AN SiH-FUNCTIONAL COMPONENT CONTAINING ORGANOSULFUR COMPOUNDS

(57) Abrégé/Abstract:

The present invention relates to compositions which crosslink to give elastomers, comprising; (A) a polyorganosiloxane (I) with at least two alkenyl groups per molecule and a metallic catalyst (IV) and (B) a polyorganosiloxane (II) with at least two silicon-bonded hydrogen atoms and an organic sulfur compound (III).



ABSTRACT OF THE DISCLOSURE

The present invention relates to compositions which crosslink to give elastomers, comprising;

- (A) a polyorganosiloxane (I) with at least two alkenyl groups per molecule and a metallic catalyst (IV) and
- (B) a polyorganosiloxane (II) with at least two silicon-bonded hydrogen atoms and an organic sulfur compound (III).

**TWO COMPONENT SILICONE RUBBER WITH IMPROVED COMPRESSION
SET PREPARED FROM AN SiH-FUNCTIONAL COMPONENT CONTAINING
ORGANOSULFUR COMPOUNDS**

5

BRIEF SUMMARY OF THE INVENTION

The present invention relates to compositions which crosslink to give elastomers, to a process for their preparation and to shaped articles produced from these compositions.

BACKGROUND OF THE INVENTION

Compositions which crosslink to give elastomers and are said to have a low compression set have already been described.

15 DE 41 00 217 (Degussa AG) discloses that thiocyanatopropyltrialkoxysilanes can bring about an improvement of the compression set in molding compositions which can be vulcanized using peroxides together with heat. The same disclosure describes that the organosilicon compounds can
20 be used either separately or in combination with a filler. DE 33 19 251 (Degussa AG) discloses the use of isothiuronium compounds in place of thiourea derivatives for vulcanizable halogen rubber mixtures. The resultant vulcanizates were found to have better strength, tensile modulus, abrasion and compression set values than comparable
25 halogen rubber mixtures without isothiuronium compounds. In EP 0 278 157 (Shin Etsu Chemical Co., Ltd.), thio-carbamyl-functional organosilanes are added, in order to improve the compression set, to rubbers which are vul-
30 canizable using organic sulfur compounds or using organic peroxides.

Other proposals for improving the compression set are based on the use of additives such as, barium peroxide, barium oxide or magnesium oxide (US 3 261 801, US 3 468 838).

and US 3 865 778), and the use of polycarbodiimidepoly-siloxane copolymers (EP 0 010 708) which give strongly colored products.

5 The above mentioned methods for improving the compression set are relevant to rubbers which may be crosslinked to give elastomers by using organic sulfur compounds or organic peroxides.

By contrast, organopolysiloxane compositions which crosslink via an addition reaction, preferably via a
10 hydrosilylation reaction of vinyl-containing siloxanes, are catalyzed by a number of platinum compounds. For improving the compression set in addition-crosslinking systems, iron-manganese spinels of the empirical formula $\text{Fe}_x\text{Mn}_2\text{O}_4$ (Wacker Silicones: EP 582 299), triazole compounds (Shin Etsu
15 Chemical Co., Ltd.: US 510 49 19), vinyl-specific organic peroxides > 0.2% by weight (Dow Corning Co.: EP 0 377 185), and transition metal chalcogenides (Bayer AG:EP 0 455 078) have been described.

The above mentioned compositions have the disadvantage
20 that they do not provide addition-crosslinking compositions which are transparent and have a low compression set.

DETAILED DESCRIPTION OF THE INVENTION

It is an object of the present invention to provide
25 compositions which do not include breakdown products, as do systems which crosslink using peroxides, are more viscous than the latter, and have a low compression set with, at the same time, high reproduceability of the compression set after storage.

30 The present invention relates to compositions which crosslink to give elastomers, comprising;

- (A) a polyorganosiloxane (I) with at least two alkenyl groups per molecule and a metallic catalyst (IV) and
- (B) a polyorganosiloxane (II) with at least two silicon-
35 bonded hydrogen atoms and an organic sulfur compound (III).

Component (A) comprises polyorganosiloxane (I). Polyorganosiloxane (I) in the novel silicone rubber compositions is a polyorganosiloxane with at least two alkenyl groups per molecule and a viscosity at 25°C which is in the
 5 range from 0.5 to 500 Pa·s, preferably from 1 to 100 Pa·s and more preferably from 7 to 25 Pa·s. Polyorganosiloxane (I) is used in amounts of between 10% and 98% by weight, preferably 20% and 80% by weight and more preferably between 50% and 80% by weight.

10 Component (A) may also include further additives as described below.

Component (B) comprises polyorganosiloxane (II), an organic sulfur compound (III), and may include polyorganosiloxane (I) and further additives as described below.

15 Polyorganosiloxane (II) in the novel silicone rubber compositions is a polyorganosiloxane with at least two Si-H groups per molecule with a viscosity at 25°C which is in the range from 100 to 1000 mPa·s, preferably from 200 to 500 mPa·s.

20 The polyorganosiloxane (I) is constructed from units of the formula



where

a is 0, 1 or 2,

25 b is 0, 1, 2 or 3,

with the proviso that at least two radicals R are present in every molecule and the sum (a + b) is < 4.

R is an alkenyl group, which can undergo a hydrosilylation reaction using a SiH functional crosslinking agent.
 30 It is advantageous to use alkenyl groups with from 2 to 6 carbon atoms, such as vinyl, allyl, methallyl, 1-propenyl, 5-hexenyl, ethynyl, butadienyl, hexadienyl, cyclopentenyl, cyclopentadienyl, cyclohexenyl, preferably vinyl and allyl.

R¹ is a substituted or unsubstituted, aliphatically
 35 saturated or aromatic, monovalent hydrocarbon radical with

from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms, examples of which are the alkyl groups, such as preferably methyl, ethyl, propyl, butyl and hexyl, cycloalkyl groups, such as cyclopentyl, cyclohexyl and cycloheptyl, aryl and alkaryl groups, such as phenyl, tolyl, xylyl, mesityl, benzyl, beta-phenylethyl and naphthyl, and halogen-substituted groups, such as 3,3,3-trifluoropropyl, o-, p- and m-chlorophenyl, bromotolyl and beta-cyanoethyl.

The alkenyl groups may be bonded at any position in the polymer chain, in particular on the terminal silicon atoms.

Polyorganosiloxane (I) may also be a mixture of different polyorganosiloxanes which contain alkenyl groups, differing for example in their alkenyl group content, in the type of alkenyl group or structurally.

The structure of the polyorganosiloxanes which contain alkenyl groups may be linear or branched. Besides monofunctional units, such as $RR^1_2SiO_{1/2}$ and $R^1_3SiO_{1/2}$, and difunctional units, such as $R^1_2SiO_{2/2}$ and $RR^1SiO_{2/2}$, branched polyorganosiloxanes also comprise trifunctional units, such as $R^1SiO_{3/2}$ and $RSiO_{3/2}$, and/or tetrafunctional units of the formula $SiO_{4/2}$, where

R and R^1 are as defined above.

The content of these tri- and/or tetrafunctional units which lead to branched polyorganosiloxanes should not significantly exceed 20 mole%. The polyorganosiloxane which contains alkenyl groups may also contain units of the formula



where both

R^2 and R^3 are as defined above for R and R^1 , and

R^4 is a bivalent organic radical, such as ethylene,

propylene, phenylene, diphenylene or polyoxymethylene.

Units of this type may be present in the polyorganosiloxane

(I) in a proportion of up to 50 mole%.

Preference is given to the use of polydimethylsiloxanes which contain vinyl groups and have the formula



where

5 a is zero or a non-negative number and

b is a non-negative number, and

the following relationships are satisfied:

50 < (a + b) < 2200, preferably 200 < (a + b) < 1000.

The crosslinker used in the addition-crosslinking of
10 the novel silicone rubber composition is polyorganosiloxane (II), which is an SiH-functional polyorganosiloxane constructed from units of the formula



where

15 c is 0, 1 or 2,

d is 0, 1, 2 or 3,

with the proviso that the sum (c + d) is < 4 and that at least two hydrogen atoms bonded to silicon are present in each molecule, and R¹ is as defined above.

20 Preference is given to the use of a polyorganosiloxane which contains three or more SiH-bonds per molecule. If a polyorganosiloxane (II) containing only two SiH-bonds per molecule is used, the polyorganosiloxane (I) which contains alkenyl groups preferably contains at least three alkenyl
25 groups per molecule.

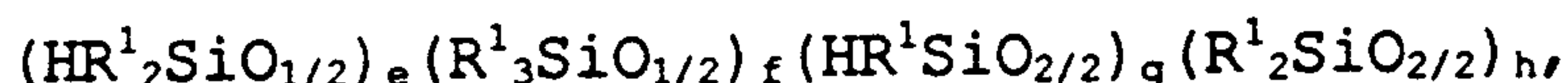
The polyorganosiloxane (II) is used as crosslinker. The hydrogen content of the crosslinker, which relates exclusively to the hydrogen atoms bonded directly to silicon atoms, is in the range from 0.002% to 1.7% by weight of
30 hydrogen, preferably from 0.1% to 1.7% by weight of hydrogen.

The polyorganosiloxane (II) contains at least three and preferably at most 600 silicon atoms per molecule. Preference is given to the use of SiH-crosslinkers which
35 contain between 4 and 200 silicon atoms per molecule.

The structure of the polyorganosiloxane (II) may be linear, branched, cyclic or network-like. Linear and cyclic polyorganosiloxanes (II) are composed of units of the formulae $\text{HR}^1_2\text{SiO}_{1/2}$, $\text{R}^1_3\text{SiO}_{1/2}$, $\text{HR}^1\text{SiO}_{2/2}$ and $\text{R}^1_2\text{SiO}_{2/2}$, where R^1 is as defined above. Branched and network-like polyorganosiloxanes (II) contain, in addition, trifunctional units, such as $\text{HSiO}_{3/2}$ and $\text{R}^1\text{SiO}_{3/2}$, and/or tetrafunctional units of the formula $\text{SiO}_{4/2}$. As the content of tri- and/or tetrafunctional units increases, these crosslinking agents show a network-like, resin-like structure. The organic radicals R^1 in the polyorganosiloxane (II) are usually selected so that they are compatible with the organic radicals in the polyorganosiloxane (I), so that the constituents (I) and (II) are miscible.

Combinations and mixtures of the polyorganosiloxanes (II) described may also be used as crosslinker.

Preferred polyorganosiloxanes (II) have the formula



where the non-negative integers e , f , g and h satisfy the following relationships: $(e + f) = 2$, $(e + g) > 2$, $5 < (g + h) < 200$, and R^1 is as defined above.

Polyorganosiloxane (II) is present in the curable silicone rubber composition in an amount giving a molar ratio of SiH groups to alkenyl groups of from 0.5 to 5, preferably from 1.0 to 3.0.

Polyorganosiloxane (II) is used in amounts of from 0.1% to 15% by weight, preferably from 2% to 8% by weight, and more preferably from 3% to 6% by weight.

The metallic catalyst (IV) which is present in component (A) serves for the addition reaction (hydrosilylation) between the alkenyl groups of the polyorganosiloxane (I) and the silicon-bonded hydrogen atoms of the polyorganosiloxane (II). A large number of suitable hydrosilylation catalysts (IV) are described in the literature. Any hydrosilylation catalyst which is conventionally

used in addition-crosslinking silicon rubber compositions may be used.

The hydrosilylation catalyst (IV) may be a metal, such as platinum, rhodium, palladium, ruthenium and iridium, preferably platinum, which optionally are supported on fine-particle carrier materials.

Platinum and platinum compounds are preferred. Preference is given to platinum compounds which are soluble in polyorganosiloxanes. Soluble platinum compounds which may be used are, the platinum-olefin complexes of the formulae $(\text{PtCl}_2 \cdot \text{olefin})_2$ and $\text{H}(\text{PtCl}_3 \cdot \text{olefin})$, where preference is given to alkenes having 2 to 8 carbon atoms, such as ethylene, propylene and isomers of butene and octene, or cycloalkenes with from 5 to 7 carbon atoms, such as cyclopentene, cyclohexene and cycloheptene. Other soluble platinum catalysts are the platinum-cyclopropane complex of the formula $(\text{PtCl}_2 \cdot \text{C}_3\text{H}_6)_2$, the reaction products of hexachloroplatinic acid with alcohols, ethers or aldehydes and/or mixtures of these, or the reaction product of hexachloroplatinic acid with methylvinylcyclotetrasiloxane in the presence of sodium bicarbonate in ethanolic solution. Preference is given to finely-divided platinum on carrier compositions such as silica, alumina or activated charcoal from vegetable or animal sources, platinum halides, such as PtCl_4 , hexachloroplatinic acid and $\text{Na}_2\text{PtCl}_4 \cdot n\text{H}_2\text{O}$, platinum-olefin complexes, for example those with ethylene, propylene or butadiene, platinum-alcohol complexes, platinum-styrene complexes as described in US 4 394 317, platinum alkoxide complexes, platinum acetylacetonates, reaction products of chloroplatinic acid with mono-ketones, such as cyclohexanone, methyl ethyl ketone, acetone, methyl n-propyl ketone, diisobutyl ketone, acetophenone and mesityl oxide, and also platinum-vinylsiloxane complexes as described, in US 3 71 5 334, 3 775 452 and 3 814 730, and platinum-divinyldimethyltetramethyldisiloxane complexes with or without

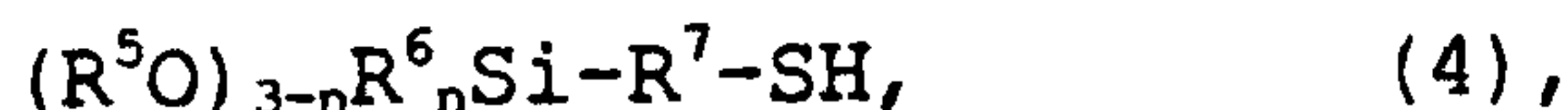
detectable amounts of inorganic halogen, in an amount which is sufficient to promote the curing of the formulation at a temperature from room temperature to 250°C, where the organohydrosiloxane and the hydrosilylation catalyst are
5 allocated to different parts of the multipart curable formulation. Preference is given to complexes of platinum with vinylsiloxanes, such as sym-divinyltetramethyldisiloxane.

The hydrosilylation catalyst (IV) may also be used in microencapsulated form, where the fine-particle solid which
10 contains the catalyst and is insoluble in the polyorgano-siloxane is, for example, a thermoplastic (polyester resin or silicone resin). The hydrosilylation catalyst may also be used in the form of an inclusion compound, for example in a cyclodextrin.

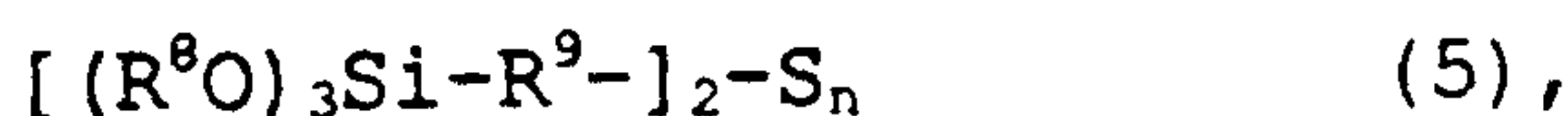
15 The amount of hydrosilylation catalyst used depends on the desired rate of crosslinking and on cost factors. If common platinum catalysts are used, the content of platinum metal in the curable silicone rubber composition is in the range from 0.1 to 500 ppm by weight, preferably from 10 to
20 100 ppm by weight of platinum metal. Otherwise, the catalyst may be used with an inhibitor, preferably in amounts of from 0.01% to 5% by weight.

The sulfur compound (III) according to the invention is an organic sulfur compound selected, for example, from
25 the group consisting of the thiols (mercaptans, such as alkylthiols and aryl thiols, mercaptoheterocyclic compounds, such as mercaptoimidazole and mercaptobenzimidazole), ketene S,X-acetals, where X is preferably N or S, thioacetals, sulfanes (thioethers), disulfanes (dithioethers), polysulfanes, thioamides, thioureas, thiurams
30 (thiurammono-, di- or polysulfides, bithiocarbamoylmono-, di- or polysulfanes), thiuronium salts, thiocarbamates, dithiocarbamates and their Zn, Fe, Ni, Co and Cu salts, thiocyanates, isothiocyanates, thiocarbonyl compounds (for
35 example thioaldehydes, thioketones, thiolactones, thio-carboxylic acids), thio-heterocyclics (for example thio-

phene, 1,2- and 1,3-dithiols and 1,2- and 1,3-di-thio-
 lethiones, thiazoles, mercaptothiazoles, mercaptothiadia-
 zoles, benzodithioles and benzodithiolethiones, benzthia-
 zoles, mercaptobenzthiazoles, phenothiazines and thianthre-
 5 nes), a silane having sulfur-containing
 functional groups, for example a mercaptoalkylalkylalkoxy-
 silane of the formula



a bis(trialkoxysilylalkyl)mono-, di- or polysulfane of the
 10 formula



a thiocyanatoalkyltrialkoxysilane of the formula



the presence of a filler, preferably silicas, onto which
 15 these silanes having sulfur-containing functional groups
 are applied, or with which the latter are reacted or
 blended, for example fine-particle-size silica, and/or the
 presence of a thio-functional siloxane, for example a poly-
 dimethylsiloxane-co-mercaptoalkylsiloxane, where alkyl is
 20 preferably ethyl and propyl, in at least one part of the
 multipart formulation, preferably in the part containing
 H-siloxane.

R^5 is a substituted or unsubstituted, aliphatically
 saturated monovalent hydrocarbon radical having from 1 to
 25 10 carbon atoms, preferably from 1 to 6 carbon atoms,
 examples of which are alkyl groups, preferably methyl,
 ethyl, propyl, butyl and hexyl, and cycloalkyl groups, such
 as cyclopentyl, cyclohexyl and cycloheptyl.

R^6 is a substituted or unsubstituted, aliphatically
 30 saturated monovalent hydrocarbon radical having from 1 to
 10 carbon atoms, preferably from 1 to 6 carbon atoms,
 examples of which are alkyl groups, preferably methyl,
 ethyl, propyl, butyl and hexyl, cycloalkyl groups, such as
 cyclo-pentyl, cyclohexyl and cycloheptyl, and aryl and
 35 alkaryl groups, such as phenyl, tolyl, xylyl, mesityl and
 benzyl.

R⁷ is a substituted or unsubstituted, aliphatically saturated bivalent hydrocarbon radical having from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms, examples of which are alkylene groups, preferably methylene, ethylene, propylene, butylene, hexylene and phenylene, more preferably propylene.

R⁸ and R¹⁰ are as defined for R⁵.

R⁹ and R¹¹ are as defined for R⁷.

n is 1 - 10, preferably 2 or 4.

10 Mixtures of these organic sulfur compounds may also be used.

The organic sulfur compound or mixtures of these is used in amounts of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.15%, based on the weight of the entire formulation.

The following additives may also be present in one of the components A or B.

While the constituents (I) to (IV) are necessary constituents of the novel silicone rubber composition, further additives may, optionally, be present in the silicone rubber composition in a proportion of up to 60% by weight, preferably from 1% to 20% by weight. These additives may, for example, be fillers, adhesion promoters, inhibitors, metal powders, fibers, pigments, dyes, plasticizers etc.

25 Examples of fillers are reinforcing fillers of a reinforcing inorganic filler, preferably of silicate type, such as fine-particle-size silica having a specific surface area of from 50 to 500 m²/g, preferably from 150 to 300 m²/g, and may also be surface-modified. They may be prepared, by precipitation from silicate solutions using inorganic acids and by hydrothermal development, by high-temperature hydrolysis and/or oxidation of volatile silicon halides, or by a luminous arc process. These silicas may, optionally, be in the form of mixed oxides or oxide mixtures with the oxides of aluminum, magnesium, calcium, barium, zinc,

zirconium and/or titanium. Use may, furthermore, be made of non-reinforcing fillers, i.e. fillers having a BET specific surface area of less than 50 m²/g, such as quartz powder, diatomaceous earth, calcium silicate, zirconium silicate, zeolites, metal oxides, such as iron oxide, zinc oxide, titanium dioxide, aluminum oxide, metal carbonates, such as calcium carbonate, magnesium carbonate, zinc carbonate, metal sulfates, mica, siloxane resins, clays, lithophones, graphite and chalk. The fillers which are described may be hydrophobicized. Use may be made of synthetic silicates, naturally-occurring silicates, glass fibers and glass-fiber products, such as mats, strands, fabrics, non-wovens and the like, and glass microbeads. It is preferable to add from 10% to 60% of filler, based on the weight of the formulation.

Carbon black may also be present in the novel rubber compositions, not only for gray or black coloration of the vulcanizates, but also to achieve particular, valuable vulcanization properties, preference being given to the carbon blacks which are known for use in rubbers. The carbon black is used in amounts of from 0 to 35 parts by weight, based on 100 parts by weight of rubber, in at least one part of the multipart formulation. For the purposes of the present invention, a lower limit of zero means that the constituent is optionally present in the rubber mixture. If carbon black is present in a mixture, the lower limit in practice is 0.1 parts by weight.

In the case of oil-bleeding elastomers, an amount of from 0% to 10% of a filler, preferably from 0.1% to 5%, based on the weight of the formulation, of an organoaryl-siloxane, preferably of a polydimethyl-co-methylphenyl-siloxane, is added. For the purposes of the present invention, a lower limit of zero means that the constituent is optionally present in the rubber mixture. If an organoaryl-siloxane is present in a mixture, the lower limit in practice is 0.1 parts by weight.

Examples of plasticizers are diorganopolysiloxanes which are liquid at room temperature, and are end-blocked by triorganosiloxy groups, such as dimethylpolysiloxanes which are end-blocked by trimethylsiloxy groups and have a
 5 viscosity at 25°C of from 10 to 10,000 mPa.s.

In particular, resin-like polyorganosiloxanes which essentially consist of units of the formulae $R^{12}_3SiO_{1/2}$, $R^{12}_2SiO_{3/2}$ and/or $SiO_{4/2}$ and optionally $R^{12}_2SiO_{2/2}$, in a proportion of up to 50% by weight, preferably up to 20% by
 10 weight, based on the total weight of the silicone rubber, may be present. The molar ratio between monofunctional and tri- or tetrafunctional units in these resin-like polyorganosiloxanes is preferably in the range from 0.5:1 to 1.5:1. Functional groups, in particular alkenyl groups in
 15 the form of $R^{13}R^{12}_2SiO_{1/2}$ - and/or $R^{13}R^{12}_2SiO_{2/2}$ - units, may also be present.

R^{12} is a substituted or unsubstituted, aliphatically saturated monovalent hydrocarbon radical having from 1 to 10 carbon atoms preferably from 1 to 6 carbon atoms, exam-
 20 ples of which are alkyl groups, such as methyl, ethyl, propyl, butyl and hexyl, cycloalkyl groups, such as cyclopentyl, cyclohexyl and cycloheptyl, aryl and alkaryl groups, such as phenyl, tolyl, xylyl, mesityl, benzyl, beta-phenylethyl and naphthyl, and halo-substituted groups,
 25 such as 3,3,3-trifluoropropyl, o-, p- and m-chlorophenyl, bromotolyl and beta-cyanoethyl.

R^{13} is an alkenyl group, which may be any alkenyl group which can undergo a hydrosilylation reaction with an SiH-functional crosslinker. It is advantageous to use alkenyl
 30 groups having from 2 to 6 carbon atoms, such as vinyl, allyl, methallyl, 1-propenyl, 5-hexenyl, ethynyl, butadienyl, hexadienyl, cyclopentenyl, cyclopentadienyl and cyclohexenyl, preferably vinyl and allyl.

Additives may be present which enable the pot life and
 35 the rate of crosslinking of the curable silicone rubber composition to be set to the desired value. Examples of

these inhibitors and stabilizers, which are known are:
acetylenic alcohols, such as ethynylcyclohexanol and
2-methyl-3-butyn-2-ol, polymethylvinylcyclsiloxanes, such
as methylvinylcyclotetrasiloxane, low-molecular-weight
5 siloxane oils with vinyl dimethylsiloxy end-groups, trialkyl
cyanurates, alkyl maleates, such as diallyl maleate and
dimethyl maleate, alkyl fumarates, such as diethyl fumarate
and diallyl fumarate, organic hydroperoxides, such as
cumene hydroperoxide, tert-butyl hydroperoxide and pinane
10 hydroperoxide, organic peroxides, benzotriazole, organic
sulfoxides, organic amines and amides, phosphines, phos-
phites, nitriles, diaziridines and oximes. Preference is
given to siloxanes, and particular preference is given to
1,3-divinyl-1,1,3,3-tetramethyldisiloxane and tetramethyl-
15 tetra vinylcyclotetrasiloxane.

The novel silicone rubber compositions are preferably
prepared by, in a first step, mixing the filler with the
polyorganosiloxane (I) containing alkenyl groups to give a
homogeneous mixture. The filler is incorporated into the
20 polyorganosiloxane in a suitable mixer, e.g. a compounder.

Components (A) and (B) are used in a weight ratio of
from 10:1 to 1:0.5, preferably of 1:1.

The invention further relates to a process in which
component (A) is mixed with component (B).

25 Components (A) and (B) are as defined above. The com-
ponents are intensively mixed at room temperature (25°C)
and atmospheric pressure. The mixture is then vulcanized
for from 0.01 to 10 min, preferably from 0.02 to 5 min, at
from 70°C to 250°C, preferably at 90°C to 180°C.

30 The invention further relates to a shaped article
which comprises novel compositions or compositions prepared
by the novel process.

The novel moldings are transparent, elastomeric mold-
ings which can be colored if required, have good to very
35 good mechanical properties and can be produced cost-effec-
tively by the novel process. Moldings of this type are

prepared by injection molding. Such moldings exhibit a lasting deformation on compression, the compression set. This deformation is especially large immediately following production, if there is no post-curing. In certain applications, e.g. gaskets in the automotive and engineering sectors where on technical or cost grounds there is often no post-curing of the moldings, it is essential in particular in the case of moldings which are not post-cured to achieve as low a compression set as possible. The invention achieves this object. However, post-curing is also possible according to the invention.

The good reproducibility of the compression set after storage if the organic sulfur compound is present in a small amount in component (B) is especially surprising. The rate of crosslinking in the novel moldings is therefore surprisingly lower than if the organic sulfur compound were present in component (A), even after relatively long storage times. This makes it possible to guarantee a shelf life of up to 6 months for the formulated product. The good shelf life therefore gives short, constant crosslinking times, which ensure fast and continuous production. This means that processing machines do not have to be repeatedly adjusted to take account of longer crosslinking times which can otherwise result from storage; this results in considerable cost savings, and because of the short cross-linking time more moldings can be produced.

The compositions which crosslink to give elastomers have a compression set, after vulcanization and without post-curing, of less than 50, preferably less than 25, and more preferably less than 10, where a value of 0 indicates no compression set at all. The compression set is measured according to DIN 53517.

It is characteristic of addition-crosslinking silicone rubbers that, in contrast to peroxide crosslinking, no breakdown products of the crosslinker are liberated. Addition-crosslinking liquid silicone rubbers also have a lower

viscosity when compared with hard silicone rubbers and other elastomers. This favorable consistency and the cross-linking method lead to numerous advantages in processing, in particular in the cost-effective mass production of small moldings. A process without after-treatment, e.g. without post-curing of the moldings, is an important factor for automated production. A low compression set is advantageous for numerous applications in the field of sealing technology, e.g. O-rings, valve-cover gaskets, sealing lips, seals in dialysis machines and disposable syringes, cisterns, etc. Oil-bleeding silicone rubbers permit easy assembly and inhibit corrosion of electrical connections resulting from external agents. In this application, as weather packs, a low compression set in addition to other excellent mechanical properties, such as high tear resistance and elongation at break, offers technical advantages. It is for these reasons that the subject of the invention is of particular interest, since the highlighted sulfur-containing additives significantly improve the compression set without any substantial effect on the other mechanical properties and/or on the crosslinking behavior.

A common feature of the compounds described in the prior art is that they are not addition-crosslinking compositions which include organic sulfur compounds. The literature warns against the use of even the smallest amounts of organic sulfur compounds in addition-crosslinking systems, because of poisoning of the catalyst in such systems. "Ullmanns Enzyklopädie der technischen Chemie" [Ullmann's Encyclopedia of Industrial Chemistry], 4th Edition, Vol. 21, p.525, Verlag Chemie, 1982, takes the same view and states that the vulcanization behavior of addition systems is sensitive to disturbance by sulfur compounds, so that great care should be taken to avoid contamination by such compounds. Furthermore, catalyst poisoning in addition systems is referred to at the following points in text books: W. Hechtel, Chemie und Technologie des kalthärtenden

Silikonkautschuks [Chemistry and Technology of RTV Silicone Rubber] in Silicone, Chemie und Technologie [Silicones, Chemistry and Technology], p. 49ff, Vulkan Verlag, 1989; Ullmann's Encyclopedia of Ind. Chem., 5th Edn., Vol. A5, p. 323, Verlag Chemie 1993, Weinheim; Ullmann's Encyclopedia of Ind. Chem., 5th Edn., Vol. A 24, p. 72, Verlag Chemie 1993, Weinheim; Ullmann's Encyclopedia of Ind. Chem., 4th Edn., Vol. 21, p. 522, 525, Verlag Chemie 1982, Weinheim.

Example 1

10 Preparation of a filler which is modified with organosulfur compounds

10 g of water, followed by 12.24 g of extremely finely divided 3-mercaptopropyltrimethoxysilane, obtainable from Wacker-Chemie as "Wacker Silan™ GF 70", are incorporated
15 into 100 g of pyrogenic silica having a BET specific surface area of 300 m²/g, obtainable from Wacker-Chemie as "Wacker HDK™ T30", with stirring, at room temperature and under atmospheric pressure, followed by post-curing for 1 hour at 80°C. Removal of reaction byproducts under reduced
20 pressure gives 106.1 g of a white powder.

Example 2

Preparation of a batch for improving compression set

In a compounder, 43.3 parts by weight of vinyl-terminated polydimethylsiloxane having a viscosity of 20 pa-s are
25 mixed with 20 parts by weight of a pyrogenic silica which has been surface-modified with hexamethyldisilazane and has a BET specific surface area of 300 m²/g, and converted to a homogeneous mixture. To this mixture are added 10 parts by weight of a modified filler of Example 1, and homogeniza-
30 tion is continued for 0.5 hours at 120°C. Finally, 26.7 parts by weight of vinyl-terminated polydimethylsiloxane having a viscosity of 20 pa-s are incorporated.

Example 3

Preparation of a batch for improvement of the compression set

10 parts by weight of octadecane-1-thiol are stirred
5 into 90 parts by weight of vinyl-terminated polydimethylsiloxane having a viscosity of 20 Pas, at a temperature above its melting temperature, and converted to a homogeneous mixture.

Example 4

10 Preparation of the basic mixture of a liquid rubber

Preparation of component A: in a compounder, 82 parts by weight of a vinyl-terminated polydimethylsiloxane having a viscosity of 20 Pas are mixed with 33 parts by weight of surface-modified pyrogenic silica having a BET specific
15 surface area of 300 m²/g, and converted to a homogeneous mixture. To 100 parts by weight of this basic silicone mixture are added 0.19 parts of a platinum catalyst, consisting of 97 parts by weight of a polydimethylsiloxane and 3 parts by weight of a platinum-divinyldisiloxane complex, and 0.07 parts by weight of ethynylcyclohexanol as
20 inhibitor, and the mixture is homogenized in a compounder. Preparation of component B: in a compounder, 82 parts by weight of vinyl-terminated polydimethylsiloxane having a viscosity of 20 pa-s are mixed with 33 parts by weight of
25 surface-modified pyrogenic silica having a BET specific surface area of 300 m²/g, and converted to a homogeneous mixture. To 100 parts by weight of this basic silicone mixture are added 4 parts by weight of a polydimethylsiloxane-co-hydromethylpolysiloxane and 0.03 parts by
30 weight of ethynylcyclohexanol as inhibitor, and the mixture is homogenized in a compounder.

The resultant curable basic silicone mixtures A and B are mixed in a ratio 1:1, pressed into sheets and vulcanized at 170°C for 10 minutes.

35 Test specimens were cut out from the cured sheets and tested, as prescribed in the indicated DIN specifications.

Example 5

Preparation of an oil-bleeding liquid rubber

2 parts by weight of a polydimethylsiloxane-co-methyl-phenylpolysiloxane are mixed in a compounder with each of the components A and B of Example 4. Press-vulcanization was carried out as in Example 4, for 5 minutes at 175°C.

Example 6

0.25 parts by weight of an α,ω -trimethylsiloxy-terminated polydimethyl/3-mercaptopropylsiloxane, prepared according to US 4 046 795, as in Example 11, and having a viscosity of about 0.25 Pas and an SH-content of about 0.1%, is mixed with 100 parts by weight of component B of Example 4, and vulcanization is carried out as in Example 4.

Example 7

1 part by weight of the batch of Example 2, corresponding to about 0.1 parts by weight of the modified filler of Example 1, is mixed with 100 parts by weight of component B of Example 5, and vulcanization is carried out as in Example 5.

Example 8

0.50 parts by weight of the batch of Example 3 are mixed with 100 parts by weight of component B of Example 5, and vulcanization is carried out as in Example 5.

Improvement of the compression set in liquid rubbers:

	Example 4	Example 6
Shore A hardness	51	49
Tear resistance [N/mm ²]	8	9.5
Elongation at break [%]	460	540
Tear propagation resistance [N/mm]	28.9	32.9
Rebound [%]	62	63
Compression set 22 h/175°C [%]	62	45
Initiation temperature [°C]	120	120
Vulcanization time t 50 [s] at 170°C	23	24
Crosslinking rate v _{max} [Nm/min]	1.29	1.21

Improvement of the compression set in oil-bleeding liquid rubbers:

	Example 5	Example 7	Example 8
Shore A hardness	49	47	47
Tear resistance [N/mm ²]	9	7.9	8.8
Elongation at break [%]	580	520	600
Tear propagation resistance [N/mm]	28	24.5	24.8
Rebound [%]	61	60	56
Compression set 22 h/175°C [%]	64	17	37
Initiation temperature [°C]	111	113	116
Vulcanization time t 50 [s] at 150°C	18	17	26

DIN Specifications

- 5 DIN 53505 - Shore A hardness
- DIN 53504 - Tear resistance, elongation at break
- ASTM D 624 - Tear propagation resistance
- DIN 53512 - Rebound
- DIN 53517 - Compression set
- 10 DIN 53529 - Initiation temperature

Claims:

1. A two-component, addition-curable silicone elastomer composition which cures to form a transparent elastomer, comprising
 - (A) a first component comprising

at least one organopolysiloxane (I) bearing an average at least two alkenyl groups per molecule, and

a metallic hydrosilylation catalyst (IV); and

 - (B) a second component comprising at least one organopolysiloxane (II) bearing on average at least two silicon-bonded hydrogen atoms, and

an organic sulfur compound (III) selected from the group consisting of alkylthiols, arylthiols, mercaptoheterocycles, ketene-S,X-acetals, thioacetals, thioamides, thioureas, thiuram di- or polysulphides, bithiocarbamoyl mono-, di- or polysulphanes, thiuronium salts, thiocarbamates, dithiocarbamates and their Zn, Fe, Ni, Co or Cu salts, thiocyanates, isothiocyanates, thiocarbonyl compounds, thia-heterocycles, silanes bearing sulphur-containing functional groups, and thio-functional siloxanes, wherein when said organosulfur compound is a silane bearing sulfur-containing functional groups, said silane is optionally applied to, reacted to, reacted with, or blended with a filler material.
2. A composition as claimed in claim 1, wherein component (B) also contains polyorganosiloxane (I).

3. A composition as claimed in claim 1, wherein the organic sulfur compound is present on a surface modified inorganic filler.
4. A composition as claimed in claim 1, wherein the organic sulfur compound is 3-mercaptopropyltrimethoxysilane, 3-mercaptopropyltriethoxysilane, a polydimethylsiloxane-mercaptopropyl compound, octadecane-1-thiol or mixture thereof.
5. A composition as claimed in claim 1, wherein the organic sulfur compound is present in amounts of from 0.0001% to 2% by weight, based on the weight of the entire composition.
6. A process for preparing the composition as claimed in claim 1, which comprises mixing component (A) with component (B).
7. A shaped article with low compression set prepared by crosslinking the composition of claim 1, wherein the shaped article has not been post cured.
8. A composition as claimed in claim 1, wherein the vulcanized composition, has not been post-cured, and has a low compression set of less than 50%.
9. A composition as claimed in claim 1, wherein X is N or S in the X-acetals of organic sulfur compound (III).