Title: ADDITIVES FOR RUBBER COMPOSITIONS

Abstract: The instant invention relates to rubber compositions comprising silica, an organosilane having at least one cyclic and/or bridged alkoxy group and a rosin-containing material. The instant invention also relates to tires comprising such rubber compositions, to methods of preparation of such rubber compositions or tires thereof, and to the use of rosin-containing materials for improving the Mooney viscosity of rubbers comprising the same (e.g. in a tire).
ADDITIVES FOR RUBBER COMPOSITIONS

FIELD OF THE INVENTION

The instant invention relates to rubber compositions comprising silica, an organosilane containing hydroxy, cyclic and/or bridged alkoxy groups, and a rosin-containing material. The instant invention also relates to tires comprising such rubber compositions, to methods of preparation of such rubber compositions or tires thereof, and to the use of such materials for improving the Mooney viscosity and mechanical properties of rubbers comprising the same (e.g., in a tire).

BACKGROUND

Silanes have been used in rubber compositions as adhesion promoters, as cross-linking agents, and as surface-modifying agents. Reference is made to, e.g., E. P. Plueddemann, "Silane Coupling Agents," 2nd ed., Plenum Press 1982. Several commonly used silanes include alkoxysilanes and organomercapto silanes, such as aminoalkyltrialkoxy silanes, methacryloxyalkyltrialkoxy silanes, polysulfanalkyltrialkoxy silanes, mercaptoalkyltrialkoxy silanes, and mercaptoalkyltrialkoxy silanes of diene based elastomers that occurs when using organomercapto silanes, such as multiple mercapto and silanol functional groups, with diene based elastomers that is the uncured viscosity of the resultant compound increases significantly. This poses a significant problem in the processing of the compound. It is indicated in this patent that the use of zinc oxide, stearic acid, and modified vulcanisation system would mitigate this problem.

Viscosity reduction of silica filled rubber compound by fatty acid blend with zinc and without zinc has been presented by Struktol as "Faster Processing of High Performance Silica Compounds" presented at Congresso Brasileiro de Tecnologia da Borracha 2012.
Examples of the use of rosin derivatives in rubber compositions include for instance those described in US 2009/0209690 and US 2009/069474.

US 2009/0209690 describes a rubber composition in which the combination of silica reinforcement and a plant-derived liquid is decarboxylated rosin. This document describes that numerous coupling agents may be used for coupling to silica, for example, polysulfanes such as gcontaining n polysulfide dbridge, e and und generally mentions organomercurialalkoxysilanes, without describing their structure. Actually, this patent excludes the use of rosin with typical acid numbers around 160 mg KOH/g and claims the use of decarboxylated rosin oils with typical acid numbers between 2 and 300 mg KOH/g.

US 2009/069474 describes a tire with a tread of rubber composition which contains zinc resinate within and on the surface of said rubber composition. An additional number of coupling agents are described as to be used in conjunction with silica. Organosilylalkoxysilanes and organosilylalkoxysilanes are mentioned as such as along with polysulfanes such as bis-3-trialkoxy silylalkyl polysulfides.

The use of rosin-containing materials in combination with organosilanes having hydroxy, cyclic and/or bridged alkoxy groups and/or blocked and/or unblocked mercapto groups in silica-containing rubber compositions has not been described. Also, the benefits of the use of rosin-containing materials in combination on 25 with organosilanes as described herein, in particular with respect to improvements of Mooney viscosity of rubber compositions has neither been described nor suggested. ed.

SUMMARY

One embodiment of the present invention relates to a rubber composition including:
(a) at least one rubber; or
(b) silica; and
(c) an organosilane having hydroxy, cyclic and/or bridged alkoxy groups; and

35bridged alkoxy groups; and

and

and

and
Another embodiment of the present invention relates to the use of a rosin-containing material selected from rosin, dimerized rosin, hydrogenated rosin, disproportionated rosin, decarboxylated rosin, and rosin ester (component D) in a rubber composition further including:

- a rubber (component A);
- silica (component B);
- an organosilane having hydroxy, cyclic, and/or bridged alkoxy groups; and

...to obtain a rubber composition having, when the rubber composition is not cured, a reduced Mooney viscosity and equivalent mechanical properties when compared to a similar uncured rubber composition without component D. D.

A further embodiment of the present invention relates to a method for preparing a rubber composition including mixing:

- (A) a rubber;
- (B) silica;
- (C) an organosilane having hydroxy, cyclic, and/or bridged alkoxy groups; and
- (D) a rosin-containing material selected from rosin, dimerized rosin, hydrogenated rosin, disproportionated rosin, and decarboxylated rosin ester.

**DETAILED DESCRIPTION**

It has now been found that the use of rosin-containing materials in combination with organosilanes leads to rubber compositions with improved properties. In particular, rosin-containing materials have been found to improve the Mooney viscosity of rubber compositions comprising silica and such organosilanes.
Accordingly, rubber compositions as described herein advantageously improve the manufacture and the properties of said rubber compositions and of products comprising the same.

Organosilanes as described herein are distinct from other organosilanes, in particular from commonly used alkoxysilyl substituted organosilanes, e.g., in the groups that are bound to the silicon atom. In one embodiment, the organosilanes as described herein may have at least one mercapto and silanol functional group.

In several embodiments, the organosilanes as described herein may have at least one mercapto and silanol functional group, which will be referred to as blocked organosilanes. The term "organosilanes" as used herein shall mean a non-polymeric, dimeric or oligomeric silane having at least one hydroxy, cyclic or bridged alkoxysilyl group, optionally with such blocked groups.

Herein, organosilanes with such blocked groups will be referred to as blocked organosilanes. The term "organosilanes" as used herein shall mean a non-polymeric, dimeric or oligomeric silane having at least one hydroxy, cyclic or bridged alkoxysilyl group, optionally with such blocked groups.

In several embodiments, the organosilanes as described herein have a least one blocked group and a least one unblocked group.

Such groups confer different properties onto the rubber compositions comprising the same than other commonly used organosilanes. For instance, organosilanes as having a blocked mercapto, to have different kinetic behaviour when compared to those organosilanes having an unblocked mercapto groups.

Without being bound into any theory, the blocked groups are expected to play an important role in the reaction mechanism. The difference in hydroxy, cyclic or bridged alkoxysilyl group is made, e.g., to the publication "Kinetics of the Silica-Silane Reaction" in Kautschuk Gummi Kunststoffe (KGK) (Apr 1 2011) 1 (pp. pp 38-43) by A. Blume and the publication "Reactive Processing of Silica-Reinforced Tire Rubber - New Insight into the Time and Temperature Dependence of Silica Rubber Interaction" by Satoshi Mihara 2009.09.
Accordingly, in several aspects the instant invention relates to a rubber composition comprising a rubber, silica, an organosilane, and a rubber-containing material. In one embodiment, the organosilanes may include diol-derived organosilanes which contain multiple mercapto and silanol functional groups. In another embodiment, the silanes contain hydroxy, cyclic and/or bridged alkoxy groups derived from hydrocarbon-based diols and/or have minimal ethoxy groups.

A rubber composition comprises a rubber, silica, an organosilane, and a rubber-containing material. This material may include a rubber compound, or a compound derived from a rubber compound, e.g., by subjecting a rubber material to, e.g., a dimerization reaction, a hydrogenation reaction, a disproportionation reaction, a decarboxylation reaction, and/or a esterification reaction.

A rubber-containing material is selected from rosin, dimerized rosin, hydrogenated rosin, and disproportionated rosin. In several embodiments, the rubber composition comprises a mixture of rosin acids, which generally include C20 fused-ring monocarboxylic acids, with a nucleus of three fused six-carbon rings and one double bond with a variable number and location, and other components in minor quantities. Examples of rosin acids include abietic acid, neoabietic acid, dehydroabietic acid, pimaric acid, levopimaric acid, sandaracopimaric acid, isopimaric acid and palustric acid. The type and relative amounts of rosin acids...
present in rosin depend, in part, on the plant species and the process of production. Rosin can be obtained from pine trees by distillation of oleoresin (the residue of distillation is known as "gum rosin"), by extraction of pine stumps (known as "wood rosin") or by fractionation of tall oil (known as "tall oil rosin"). Tall oil rosin may be particularly used. Other rosin-containing materials obtained during the production of tall oil rosin such as distilled tall oil (DTO), tall oil fatty acid (TOFA) and crude tall oil (CTO) may also be used. All of these sources of rosin are examples of rosin-containing materials suitable for use in the compositions and methods described herein, which are known in the art and are commercially available. Sources of rosin may contain major components other than rosin acids. In particular, DTO, CTO and TOFA are mixtures of fatty acids and rosin acids, i.e., comprising fatty acids as major components in addition to rosin acids. The composition of DTO and CTO is described in more detail below.

Each of the terms "dimerized rosin", "hydrogenated rosin", "disproportionated rosin" and "decarboxylated rosin" refers to rosin (i.e., a mixture of rosin acids as defined above), which has been subjected to the dimerization reaction, the hydrogenation reaction, the disproportionation reaction and the decarboxylation reaction respectively. The production of these types of rosin-containing material is known in the art.

The term "rosin ester" refers to an ester of rosin (i.e., a mixture of rosin acids as defined above) and at least one alcohol. Suitable alcohols for esterification include monomono- to 30 alcohols, such as methanol, ethanol, butanol, C8-11 iso alcohols such as isodecyl alcohol and C8-12 ethylhexanol, and polyols such as diethylene glycol, triethylene glycol, glycerol, pentenyl, sorbitol, neopentyl glycol, 1,3 propanediol and trimethylol propane. In particular, useful alcohols include diethylene glycol, triethylene glycol, 1,4-pentanediol, glycerol, pentenyl glycol and 1,3 propanediol. Rosin esters may also be obtained from rosin and alcohols by methods known in the art. For example,
pie, reference is made to the processes described in the patent document US 5,504,152, which is incorporated herein by reference.

In general, rosin is esterified by a thermal reaction of rosin acids contained therein with one alcohol (i.e., one or more alcohols). In order to drive such esterification reactions to completion water may be removed from the reactor, by, for instance, distillation, application of vacuum, and other methods known to the skilled person.

The rosin-containing material may generally comprise from 1 wt.% to 99.99 wt.% of rosin compounds. The remaining of the rosin-containing material to 100 wt.% consists of components other than rosin compounds, including, for instance, fatty acids (e.g., stearic acid, oleic acid, linoleic acid, linolenic acid and pinolenic acid); high molecular weight alcohols (e.g., fatty alcohols and sterols); alkyl hydrocarbon derivates; residual terpene monomers such as α-pinene, β-pinene and other mono and bicyclic terpenes; other unsaponifiables; and trace metals.

The exact composition of rosin-containing materials may vary. For instance, the composition of wood rosin, gum rosin, tall oil rosin, tall oil (TOR), distilled tall oil (DTO), and crude tall oil (CTO) may vary depending on the starting materials and processing steps used in their production. These will also influence the composition of rosin-containing materials derived therefrom (e.g., dimerized rosin, hydrogenated rosin, indisproportionated rosin, decarboxylated rosin, and rosin ester).

A wood rosin may particularly comprise 75-99.9 wt.% (in particular 88.85-98.9 wt.%) of rosin acids, 2-5 wt. % of fatty acids, 2-10 wt.% of monoterpenes and diterpenes, and other components its to a total of 100 wt.%, including, for instance, any of the additional components described above, up to the present in rosin in particular 88.85-98.9 wt.% of other acids and unsaponifiables.

A gum rosin may particularly comprise 75-99.9 wt.% (in particular 88.85-98.9 wt.%) of rosin acids, 2-5 wt. % of fatty acids, 2-10 wt.% of monoterpenes and diterpenes, and other components its 35 to a total of 100 wt.%, including, for instance, any of the additional components described above, up to the present in rosin in particular 88.85-98.9 wt.%.
components as described above and, in particular, other acids and unsaponifiables.

A tall oil rosin may particularly comprise 575-99 wt.% in (in particular, a) 80-95 wt.% of o rosin acids, dS2-10 wt.% of fatty ty 5acids, dS and another components to total α of 100 wt.%, including, e.g., "any" of the additional 10 components as described above and, in particular, another acids and unsaponifiables. es.

A distilled tall oil rosin may particularly comprise is 10-40 wt.% of o rosin acids, dS from c50 to t80 wt.% of fatty ty acids, dS and another components to total α of 100 wt.%, including, e.g., "any" of the additional 10 components as described above and, in particular, another acids and unsaponifiables. es.

A crude tall oil rosin may particularly comprise is from c10 to 50 wt.% of rosin acids, dS from c40 to t70 wt.% of fatty ty acids, dS and another 10 components to total α of 100 wt.%, including, e.g., "any" of the additional 10 components as described above and, in particular, another acids and unsaponifiables. es.

Rosin-containing materials as described therein may generally have an acid number of from c0.5 to t190 mg m KOH/g, /g in in 2 particular a from c0 to t185 mg m KOH/g, /g more in particular a from c1.5 to t180 mg m KOH/g, /g yet more in particular a from c0.5 to t175 mg m KOH/g. The acid number can be determined according to ASTM D4651 using a standard titration with sodium hydroxide solution. on.

Rosin-containing materials as described therein may be be 25 viscous liquids or may be solids at room temperature. re Viscoosous liquids may generally have a Brookfield viscosity of at most c5000 cps, in particular of at most c10000 (cS, p and more) in particular of at most c500 (cS) at 50 °C, °C measured (by methods of known in the art). Rosin-containing materials solid at room temperature are 30 may gener ally have a softening point from c40 to t7017 °C, °C in particular from c45 to t61016°C, °C more in particular from c50 to t51016°C, °C, yet/more in particular from c0.5 to t14514°C. The ysoftening point can be measured (by the Ring and Ball method 10°C (ASTM: T28-97),7), whereby to sample of the rosin-containing material is poured mol of 1-35 ten.g into a metal ring, and is subsequently cooled. ec The ring ring is cleaned in such a way that the rosin-containing material fills it.
the ring, a steel ball is placed resting on top of the resin. The ring and ball are placed in a bracket which is lowered into a beaker containing may liquid (e.g., water, glycerol or silicone) oil depending on the expected softening point. The solvent is heated at 5°C per minute while being stirred. When the ball all drops completely, the temperature of the solvent is recorded as the ring. Ball softening point.

The properties of the rosin-containing materials may vary, and may depend on the specific type of rosin-containing material. For instance, dimerized rosin, hydrogenated rosin, and deoxybuted rosin in andro rosins may be obtained depending on the starting source of rosin, and specific preparation conditions.

Rosins may have an acid number of from 125 to 190 mg KOH/g, in particular from 140 to 180 mg KOH/g, and 20 g/ton (e.g., from 150 to 175 mg KOH/g) and have a softening point from 40 to 100°C. Dimerized rosin may have an acid number of from 120 to 190 mg KOH/g, in particular from 130 to 180 mg KOH/g, and 25 g/ton (e.g., from 135 to 175 mg KOH/g) and a softening point from 60 to 160°C. Hydrogenated rosin may have an acid number of from 140 to 180 mg/g, KOH (and a softening point from 40 to 80°C).

Disproportionated rosin may have an acid number of from 130 to 180 mg KOH/g, in particular from 140 to 165 mg KOH/g, and a softening point from 40 to 90°C and 45 to 85°C. Decarboxylated rosin may have an acid number of from 10 to 35 mg KOH/g, in particular from 25 to 125 mg KOH/g. Generally, lydecarboxylated rosin can be used.
Rosins are viscous liquids at room temperature and may particularly have a Brookfield viscosity of at most 1000 cps at 50 °C."C, as measured by methods known in the art. rt.

Rosin esters may have a van acid in number from 0.50 to 1000 5mg KOH/g. A in particular, if from 0.1 to 20 5mg KOH/g, /more in particular if from 0.1 to 7.5 5mg KOH/g and in particular softening point from 80 °C to 130 °C. A in particular /from 45 °C to 125 °C. The softening point may vary depending non of polyalcohols used in the preparation of rosin esters. Whether rosin esters are further modified, ed., 10 by, for example, dimerization (and/or fortification with for example) maleic anhydride (or of fumaric acid) has been applied. Ed Reference cis is made to, e.g., Naval Stores, etc. [Zinkel (and)] [Russell 1989, 8 Chap. 9 App. 282-285. 35.

Rosin-containing materials are generally present in rubber compositions /as described herein in amounts from 0.001 to 75-75 parts per hundred (phr) in particular from 0.01 to 75 phr, /more in particular /from 0.1 to 7.5 phr, /more in particular from 0.25 to 2 phr, /more in particular from 0.5 to 5 phr.

The term "parts per hundred (phr)" of rubber composition refers to weight parts of ca. component by weight of rubber. The weight is calculated on the total amount of rubber used, e.g., if a mixture of rubbers is used, the phr is calculated on the basis of the total weight of rubber used in the mixture, etc.

The amount of rosin-containing material is present in rubber compositions as described herein in amounts by weight of organosilane and polyalcohols used in the material from 0.1 to 100% wt. % based on total weight of rubber. In particular, the amount of rosin-containing material is present in rubber compositions from 0.5% to 75% wt. %, /more in particular /from 2.5% to 7.5% wt. %, /more in particular /from 5% to 50% wt. %, /even /5% to 35% in particular /from 0.1% to 70% wt. %, /yet /more in particular from 0.5% to 25% wt. %.
A rubber composition as described herein may comprise any type of rubber selected from natural and synthetic rubbers, including solution or emulsion polymerizable elastomers.

Suitable rubbers include polymers of at least one monomer selected from olefin imonomers, including: monoolesfins such as ethylene, propylene; nonconjugated diolefins such as isoprene and butadiene; triolefins; and aromatic vinyls such as styrene and alpha methyl styrene.

Natural rubber is also known as India rubber or caoutchouc and comprises polymers of isoprene as its main component. Natural rubber is generally obtained from trees of the species Hevea Brasiliensis, from Guayule dandelion, and Russian [Dandelie]-li-on.

Solution and emulsion polymerization of elastomers are well known to those of ordinary skill in the art. For example, conjugated diene monomers, monovinyl aromatic monomers, triene monomers, and the like, can be anionically polymerized to form, e.g., polymers, copolymers and terpolymers thereof.

In particular, suitable rubbers may be selected from at least one of natural rubber (NR), polybutadiene (BR), polyisoprene (IR), styrene/butadiene (SBR), styrene/isoprene (SIR), isobutylene/isoprene (IRI), isoprene (IP), polybutadiene, polyisoprene, polyisobutylene, polyacrylic (AC), polyethylene, polypropylene, polyethylene-propylene, polyethylene-propylene-diene, polychloroprene (CR), chlorinated rubber (CHR), chloroprene, chlorinated polyethylene, chlorosulfonated polyethylene, fluorostyrene, fluoroelastomers, tetrafluoroethylene-propylene, epichlorohydrin rubbers, and silicone rubber.
Further, suitable rubbers include the above mentioned rubbers which additionally have functional groups, such as carboxyl groups, silanol groups, siloxy groups, epoxide groups, and amine groups. The functionalization of rubbers is well-known in the art. Examples of functionalized rubbers include, for instance, epoxidized natural rubber, carboxy-functionalized NBR, silanol-functionalized (SiOH)SBR, siloxy-functionalized (Si-OR)SBR, amine-functionalized SBR. Such functional rubbers may react with the silica and silanes present in the rubber composition. However, non-functionalized rubbers may also be particularly used.

In particular, rubbers may also be selected from at least one of styrene/butadiene copolymer (SBR)BR, natural rubber, polyisoprene, neoprene, styrene/isoprene/butadiene terpolymer (SIBR)BR, and isoprene/styrene copolymer; even more in particular, from at least one of styrene/butadiene copolymer (SBR)BR, polybutadiene (BR), and natural rubber. A composition as described herein may comprise a mixture of two or more rubbers as described above. In particular, component (A) of a composition as described herein may be a mixture of any one or more of styrene/butadiene copolymer (SBR)BR, natural rubber, polyisoprene, neoprene, styrene/isoprene/butadiene terpolymer (SIBR)BR, and isoprene/styrene copolymer. More in particular, a rubber mixture may comprise at least two of styrene/butadiene copolymer (SBR)BR, polybutadiene (BR), and natural rubber.

Polybutadienes (BR) may also be selected from high cis 1,4- 30 polybutadiene and high vinyl γ polybutadiene. A high vinyl γ polybutadiene generally has a vinyl γ content ranging from 30 to 99.9 wt.%, wherein γ is the weight percentage (wt.%) and is based on the total weight amount of polybutadiene. A high cis 1,4-polybutadiene may generally have a cis 1,4-butadiene content ranging from 90-99.9 wt.%, and on 35 the total weight amount of polybutadiene. In several embodiments, 1-
ments, a polybutadiene may be a high cis 1,4-polybutadiene with 99.5 wt.% of cis 1,4-butadiene monomer.

Polyisoprenes \( \text{IR} \) may be cis 1,4-polyisoprene (natural and synthetic). Polyisoprenes (IR) may be cis 1,4-polyisoprene (natural and synthetic).

Styrene-butadiene copolymers \( \text{SBR} \) may be derived from an aqueous emulsion polymerization or a solution polymerization. \( \text{SBR} \) may be particularly used. An example of commercially available solution-polymerized \( \text{SBR} \) (oil extended) is Duradene™ from Firestone Polymer.

A SBR (either E-SBR or S-SBR) may have styrene contents of from 1 to 60 wt.%, particularly from 5 to 50 wt.%, wherein in the weight percentage \( g \) (wt.%), \( g \) is based on the total weight \( m \) (wt.%) of \( SBR \).

Acrylonitrile/butadiene copolymers \( \text{NBR} \) may have acrylonitrile contents of from 5 to 60, preferably 11 to 50 wt.%, wherein in the weight percentage \( g \) (wt.%), \( g \) is based on the total weight \( m \) of \( NBR \).

Rubber compositions as described herein comprise silica, which acts as reinforcing filler.

Silica may be selected from at least one of amorphous silica, precipitated silica, wet silica, dry silica, and fumed silica. The silica can also be in the form of mixed oxides with other metal oxides, such as aluminum oxide, magnesium oxide, calcium oxide, barium oxide, zinc oxide, and titanium oxide.

In several embodiments, the silica may be amorphous silica, precipitated silica, and highly dispersible silica.

Examples of suitable commercially available silicas include: Hi-Sil™ 190, Hi-Sil™ 210, Hi-Sil™ 235, Zeosil™ 1085GR, Zeosil™ 1115MP, and Zeosil™ Premium 200 from Solvay; and Zeopol™ 8745 and 8755 LS from Huber.
A silica may generally have a specific surface area (BET surface area) from 5 to 1000 m²/g, in particular from 10 to 750 m²/g, or more in particular from 25 to 500 m²/g, or even more in particular from 50 to 250 m²/g, and may generally have a particle size from 10 to 500 μm, in particular from 50 to 250 μm, or more in particular from 75 to 150 μm. Methods of measuring the silica surface area and particle size are well known in the art. In particular, a silica surface area may be measured by the commonly used BET method of.

The pH of a silica may generally be from about 5.5 to about 7 or slightly over, preferably from about 5.5 to about 6.8. A rubber composition described herein may generally comprise silica in an amount from 0.5 to 150 phr, in particular from 25 to 130 phr, or more in particular from 40 to 115 phr.

A rubber composition described herein may comprise additional fillers other than silica, such as carbon black; metal oxides; hydroxides (e.g., aluminum hydroxide); silicates such as aluminum silicate; 100% natural rubber; and a mixture thereof of In particular, a rubber composition described herein may comprise both silica and carbon black or both silica and aluminum hydroxide as the filler.

When present, additional fillers may be present in rubber compositions in amounts from 0.5 to 40 phr, in particular from 10 to 20 phr, and, in particular, from 10 to 20 phr. The amount of additional fillers may be chosen based on the desired amount of silica present in the rubber compositions as described above. The additional filler may be present in a weight ratio of (additional filler to silica) from 70:30 to 1:99, or more in particular from 50:50 to 10:90, or more in particular from 40:60 to 20:80.
Rubber compositions as described herein comprise an organosilane having at least one hydroxyl, cyclic and/or bridged alkoxy group, up and/or at least one blocked mercapto group, up and/or at least one unblocked mercapto group, up. In another embodiment, organosilanes as described herein have at least one blocked mercapto group, at least one blocked group and at least one unblocked group. In another embodiment, organosilanes as described herein have at least one blocked mercapto group and at least one unblocked mercapto group and at least one hydroxyl, cyclic and/or bridged alkoxy group.

In another embodiment, the organosilane may be the product of reacting a hydrocarbon-based diol (e.g., 3-methyl-1,3-propane diol) with the $S-[3-(triethoxysilyl)propyl]thiooctanate$ as referred to in US Patent No. 8,609,877 which is incorporated herein in its entirety. It is considered herein that at alternately, said organosilane may be the product of said diol and $S-[3-(trichlorosilyl)propyl]thiooctanate$.

In another aspect, it is envisioned herein that such organosilane may be comprised of, for example, 1 a generalised illustrative structure (I):

\[
\text{(I)}
\]

Wherein $R^1$ is a hydrocarbon radical containing from 4 to 10 carbons, preferably an alkyl radical and preferably containing 7 carbon atoms; and

Wherein $R^2$ is an alkylene radical containing from 3 to 6 carbon atoms, preferably 4 carbon atoms;
Wherein \( R^3 \) is an alkylene radical containing from 3 to 8 carbon atoms, preferably 4 carbon atoms;

Wherein \( R^4 \) radicals are the same or different alkyl radicals containing from 3 to 8 carbon atoms;

Wherein \( R^5 \) radicals are:

(a) The same or different alkyl radicals containing from 3 to 8 carbon atoms,

(b) Combined to form an individual alkyl radical, \( R \), which may be branched or unbranched alkyl radical, having from 3 to 8 carbon atoms.

Wherein \( z \) is a value in the range of from 0 to 6.

Wherein the total of \( x \) and \( y \) is at least 1, which may be, for example, from 3 to about 15 or more; and

Wherein \( m \) and \( n \) are each values in a range of from 0 to 8.

It is contemplated that the various alcohol groups are reactive with hydroxyl groups, for example, on the precipitated silica and further, because they contain more than 2 carbon atoms, do not liberate ethanol (as a by-product) upon reacting with the said hydroxyl groups on the said immobilized silicas.

Oligomeric organosilanes described herein are discussed in "NXT™ Silane Processing and Properties of a New Virtually Zero VOC Silane" by D. Gurovich, et al., presented at the Fall 2011 Technical Meeting of the Rubber Division, American Chemical Society, on Oct. 10-12, 2011 at Cincinnati, Ohio, which presentation is incorporated herein in its entirety.

Oligomeric organosilanes described herein are discussed in "GE's New Ethanol Free Silane for Silica Tires" report by A. Chaves, et al., presented at the 2006 ITEC (Year: 2006) Conference on Set. 11-12, 2006 (Paper: 28B) at Akron, Ohio, which refers to NXT™, which presentation is incorporated herein in its entirety.

Oligomeric organosilanes described herein are set forth in US Patent Nos. 8,008,519; 8,158,812; 8,609,877; 7,718,819; 7,827,844;
and the entire subject matter of which is incorporated herein by reference. c.e.

Organosilanes as described herein are generally present in the rubber compositions in amounts from 0.05 to 75 phr, in particular from 0.1 to 60 phr, more in particular from 0.5 to 50 phr, even more in particular from 1 to 30 phr, and yet more in particular from 5 to 15 phr.

The amount of organosilane may be based on the total weight amount of silica present in the rubber composition, in particular from 5 to 30 wt.%, more in particular from 10 to 20 wt.%.

In several aspects, the instant invention relates to rubber compositions comprising:

(A) [rubber];
(B) [5-150 phr] of silica; and
(C) [0.05-75 phr] of an organosilane; and
(D) [0.001-75 phr] of a rosining-containing material; wherein (A) is in the weight parts of each component in (B), (C) or (D) [per 100 weight parts of rubber component in (A)].

The amounts of each of the components may be varied as indicated above when describing each of the different components, in particular in rubber compositions in may comprise any combination of the specified amounts mentioned above for each of the components.

A rubber composition as described herein may comprise additional ingredients other than a rubber (A) silica; c. (B) organosilane; and (C) rosin-containing material; and (D).

The amount and type of additional components, if any, may depend on the final application of the rubber composition. Suitable additional components include, for instance, curing agents like 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane (DTBPH) or dicumyl peroxide (DCP); curing or vulcanizing agents like sulphur, ur,
Vulkacit C S 1.5, Vulkacit D from Lanxess, Rhenogran IS 60-75 from Rheinchemie) as activators with maleimide groups (e.g., 1,3-bis(4-tert-butylcatechol) B(4TBC) methyl disubstituted aminoalkylenphenols as 5- and hydroperoxides, accelerators (e.g., 2-mercaptobenzothiazole (MBT), 1,4-cyclohexyl-2-benzothiazylsulphenamide (CBS) or TMTD and ind sulphur) as dispersing and processing aids like oils (e.g., TDAE, Vivatec™ 500 purchased from Hansen & Rosenthal) as resins, plastizers and pigments; fillers other than silica (such as those described above, e.g., Carbon Black); fatty acids (e.g., stearic acid); zinc oxide; waxes (e.g., Antilux™ 654 from Rheinchemie); antioxidants (e.g., IPPD, Vulkanox™ 4010 and 4020 from Lanxess); antiozonants (e.g., Durazone® 373 from SpecialChem) as peptizing agents (e.g., diphenylyguanidine, SDGP, GP, Vulkacit™ tGIS 607537 from Rheinchemie).

Several aspects of the instant invention also relate to methods of preparation of rubber compositions as described herein. A method for preparing the rubber composition as described herein may comprise mixing:

(A) rubber; (B) silica; (C) organosilane having at least one hydroxyl, cyclic and/or bridged alkoxy group; and (D) rosin-containing material selected from: rosin, di- or trimerized rosin, hydrogenated rosin, disproportionated rosin, decarboxylated rosin, and rosin ester.

Rubber compositions as described herein may be compounded or blended by using mixing equipments and procedures as conventionally employed in the art. The different components at (A) to (D) may be mixed in any order.

What has been described above for the rubber composition, on regarding the individual amounts of the different components and in particular examples of each of the components, also applies to the method of preparation as described herein.
In several embodiments, an initial master batch may be prepared including or all, generally all, of the rubber or component in (A) (and an additional component selected from: all or part of the silica component in (B) and all or part of the organosilane component in (C), a) all or part of the herosin-containing material or component in (D) and a swellable other optional non-curing ingredients, such as processing oil, antioxidants and other non-curing ingredients, commercially available in the art.

After the master batch is prepared, one or more optional stages can follow, in which either no or ingredients are added to the first mixture, or part of all of the remaining portion of the silica component, the organosilane component, the herosin-containing material or component, swellable other non-curing ingredients are added to the first mixture.

The master batch products obtained in the subsequent remill steps are commonly referred to as non-productive rubber compositions. Non-productive rubber lacks any curing agents (also referred to in the art as vulcanizing agents), and therefore no cross-linking will occur.

The next step may be the addition of curing agents to the mixture, to provide a known in the art as a productive rubber composition. This productive rubber composition will lead to a cross-linked rubber composition when subjected to a curing cycle or vulcanizing conditions. Herein, in the art cross-linked rubber composition will be preferred to as a cured rubber composition, of which in the art is also known, was vulcanized rubber composition. Accordingly, by the method of preparation cited as described herein may be further comprised of curing aided productive rubber compositions to provide as a cured rubber compositions.

A rubber may be pre-treated prior to being mixed with other components of the composition as described herein. For instance, a rubber may be an oil-containing rubber, i.e., rubber which has been pre-treated with extender oil, or in solution master batch rubber in which the silica is pre-dispersed in the rubber er. Such pre-treated rubbers are described in the literature and generally are commercially available. For instance, U.S. Patent...
No.7,312,271 describes the preparation of a solution masterbatch rubber containing a diene elastomer in an organic solvent and a reinforcing silica filler dispersed therein. The article "Silica wet masterbatch" by Lightsey et al in the June volume of Rubber World 1998 describes a process that essentially completes incorporation of silica during coagulation of traditional SBR or other latex. Suitable pre-treated rubbers include commercially available rubbers such as rubbers for shoe soles and for tire treads, compounds for tires for trucks and passenger cars. Silica may also be pre-treated prior to being mixed into to other components of the rubber composition as described herein. Alternatively or additionally silica may be pre-treated with sulfur-containing coupling agents 15other silicon organosilanes as described herein. In the art, pre-treated silica is commercially available and/or may be prepared by known methods. For instance, US patent No.5,985,953 describes a compatibilized silica formed by the reaction of precipitated or fumed silica with organosilicon coupling compounds in aqueous suspension. US patent No.6,288,474 describes mercaptoalkylsilanes rebound into silica and blocked mercaptoalkylsilanes rebound into silica. Reference is also made to the publication "PPG's Agilon silicas: eliminate silanisation and outgassing" in the European Rubber Journal Vol. 191, No. 2, March/April 2009, page 12. Particular examples of commercially available pre-treated silicas include Ciptane™ 255LD, LD, which is a mercaptoalkylsilane fixed to silica with virtually no trialkoxysilane present, or Agilon™ 2400 and 30Hi-Sil™ from Pittsburgh Paint & Glass. When silica is pre-treated with a organosilane as described herein, it is used, e.g., in a part of the rubber composition as described herein may be added to the rubber composition in the form of said pre-treated silica. ca.
It has been found that rubber compositions as described herein have advantages both as uncured rubber compositions and as cured rubber compositions. Accordingly, in several embodiments the rubber compositions described herein may be uncured rubber compositions or cured rubber compositions. In several particular embodiments uncured rubber compositions may be non-productive or productive uncured rubber compositions.

Advantageously, rubber compositions as described herein in improve the manufacture and the properties of products comprising the same. In particular, rosin-containing materials as described herein may be used to provide uncured rubber compositions with reduced Mooney viscosity and equivalent mechanical properties, when compared to similar uncured rubber compositions without rosin-containing materials as described herein. The term "similar composition" means a comparison composition of the invention in all its components and regards to the selection of materials and amounts thereof, without containing any of the rosin-containing materials as described herein. In particular, mechanical properties, when compared to similar uncured rubber compositions do not contain any of the rosin-containing materials, which is the same as the composition of the invention. Rubber compositions as described herein in particular uncured rubber may display a Mooney viscosity which is from 15 to 65% lower, or in particular, from 20 to 60% lower, in particular, from 20 to 50% lower, or even from 40 to 40% lower, or in the Mooney viscosity obtained for a similar composition without any rosin-containing materials, as the Mooney viscosity may be determined according to procedures described in ASTM-D-1646-89 (ISO 289). For uncured rubber the Mooney viscosity may be measured at 100°C. Rosin-containing materials as described herein may also be used to provide rubber compositions, or cured or uncured, in particular uncured, and all tensile mechanical properties which are at least as good, or when compared to
similar rubber compositions without rosin-containing materials as described herein. The tensile mechanical properties of the rubber can be measured using standard procedures such as those described in ASTM D746-10 for uncured rubber and in ISO 37 for cured rubber. Parameters commonly used in the art which may be measured include the tensile strengths measured at 50%, 200%, and 300% elongation on (M500), (M200) and at a 300% elongation on (M300); the tensile strength at break (TB) and the elongation at break (EB). The M300/M100 ratio gives an idea of the reinforcement properties of the rubber composition. Rosin-containing rubber compositions as described herein give similar tensile strengths and elongation at break results as rubber compositions without rosin-containing materials as described herein.

Rosin-containing rubber compositions as described herein also provide rubber compounds where the vulcanisation properties are unaffected when compared to similar rubber compositions without rosin-containing materials as described herein. The cure properties of the rubber can be measured using standard procedures such as those described in ISO 6502. Parameters commonly used in the art which may be measured include the minimum force or torque, ML, the maximum force or torque, MLH, and the time into a percentage of full cure, e.g., 90% (TC90). Rosin-containing rubber compositions as described herein give similar vulcanisation properties as rubber compositions without rosin-containing materials as described herein. The cured resilience properties of the rubber can be measured using standard procedures such as those described in ISO 4662. Parameters commonly used in the art which may be measured include the rebound resilience as a percentage at different temperatures, e.g., 23°C and 60°C. Rosin-containing rubber compositions as described herein give similar vulcanisation properties as those described in the art.
properties as rubber compositions without rosin-containing materials as described herein.

Rosin-containing rubber compositions as described herein also provide rubber compounds where the cured hardness properties are unaffected when compared to similar rubber compositions without rosin-containing materials as described herein. The cured hardness properties of the rubber can be measured using the Shore A method. Rosin-containing rubber compositions as described herein give similar hardness properties as rubber compositions without rosin-containing materials as described herein.

Several aspects of the instant invention relate to the use of a rosino-containing material selected from rosins, dimerized rosins, hydrogenated rosins, disproportionated rosins, decarboxylated rosins, jester rosins (component D), silica (component B), and organosilane having cyclic and/or bridged alkoxy groups (component C) to obtain a rubber composition having, when the rubber composition is not cured, a reduced Mooney viscosity when compared to a similar uncured rubber composition without component D; and/or to obtain a rubber composition having, when the rubber composition is cured, suitable rolling resistance when compared to a similar cured rubber composition without component D.

The methods of preparation as described herein may result in rubber compositions having any of the properties as described above for the rubber composition, or what has been described above for the rubber composition, or in particular:

- the individual amounts of the different components;
- particular examples of each of the components; and
- regarding the Mooney viscosity, mechanical properties (such as M300/M100 ratio, elongation at break, and tensile strength at break) also apply to the rubber of the uses, etc., methods of preparation and applications as described herein.
Rubber compositions as described herein may be used in numerous applications, such as tires and industrial rubber goods (e.g., conveyor belts, and shoe soles).

In particular, rubber compositions as described herein, in particular, can be advantageously used in tires, and in particular, in tire treads. Accordingly, in several aspects, the invention relates to a tire comprising a rubber composition as described herein, and to a tire comprising a rubber composition as described herein, in the tread of the tire.

A tire comprising a rubber composition as described herein may generally comprise other components in addition to rubber (A), silica (B), organosilane (C) and rosin-containing material (D). Examples of additional components include, among others, of the additional components that may be present in the rubber composition as described herein.

Other aspects of the invention also relate to a method for maintaining the mechanical properties of cured rubber compositions, in particular, for maintaining the mechanical properties of a tire while improving the processing conditions, such as tires as the he 20 viscosity, thereby wherein the tire comprises a rubber composition as described herein.

In particular, the invention relates to the use of a rosin-containing material selected from rosin, dimerized rosin, hydrogenated rosin, disproportionated rosin, decarboxylated rosin, and rosin ester (component D) to obtain a rubber composition having, when the rubber composition is cured, desirable mechanical properties (e.g., tensile strength), wherein the rubber composition further comprises as rubber (component A) A; silica (component B) B; and organosilane having at least one hydroxy, cyclic, and/or bridged alkoxy group (component C) C. In particular, an embodiment of the rubber composition as described herein is comprised of a tire.

The invention is further illustrated with the following examples, without being limited thereto or thereby.
Preparation of rubber compositions

Rubber compositions were prepared with the formulations as detailed in Table 1.

The rubber compositions prepared differed in the type of organosilane used and if rosin-containing material was used (component D) in Table 1 or not:

<table>
<thead>
<tr>
<th>Component (PHR)</th>
<th>Comp. Ex. 1</th>
<th>Ex. 2</th>
<th>Ex. 3</th>
<th>Ex. 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Rubber</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>(B) Silica</td>
<td>80.0</td>
<td>90.0</td>
<td>80.0</td>
<td>80.0</td>
</tr>
<tr>
<td>(C) Organosilane</td>
<td>5.3</td>
<td>5.3</td>
<td>5.3</td>
<td>5.3</td>
</tr>
<tr>
<td>(D) Rosin-containing material</td>
<td>0</td>
<td>1.0</td>
<td>0.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 1: Additional components (PHR)

<table>
<thead>
<tr>
<th>Component</th>
<th>Ex. 1</th>
<th>Ex. 2</th>
<th>Ex. 3</th>
<th>Ex. 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral Oil</td>
<td>31.3</td>
<td>31.3</td>
<td>31.3</td>
<td>31.3</td>
</tr>
<tr>
<td>Vulcanization package</td>
<td>10.7</td>
<td>10.7</td>
<td>10.7</td>
<td>10.7</td>
</tr>
<tr>
<td>Carbon black</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Antioxidants</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Wax</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The rubber used consisted of a mixture of rubbers comprising 70 parts of Solution Styrene-Butadiene Rubber (S-SBR) BR 15 (BunaVSL, GR, obtained from Lanxess), 30 parts of Butadiene Rubber BR (BunaR CB24™, obtained from Lanxess), and precipitated silica (Ultrasil™ 7000GR, GR, obtained from Evonik).

In Examples 1 and 2, the rosin-containing material was Tall Oil Rosin having a softening point of 63 ℃ and an acid number of 168 mg KOH/g.

In Examples 1 and 2, the organosilane was the Mercapto-thiocarboxylate Oligomer NXT Z45 purchased from Momentive.
In Examples 3 and 4, the organosilane was the Mercapto-thiocarboxylate Oligomer NXT, purchased from Momentive. The carbon black (CB) was Corax™ XN330, purchased from Orion Engineered Carbons.

The mineral oil Treated Distillate Aromatic Extract (TDAE, Vivatec™ 500) was purchased from Hansen & Rosenthal.

The antioxidants used was 2 phr of N-(1,3-dimethyl-butyl)-N' phenyl-p-phenylenediamine (6PPD, Vulkanox™ 4020) purchased from Lanxess.

The wax was Antilux™ 654, purchased from Rheinchemie, Germany.

The vulcanization package consisted of 2.5 phr of zinc oxide (Zinc Oxide Red Seal™ purchased from Grillo), 2 phr of stearic acid, 2 phr of N-cyclohexyl-2-benzothiazole sulfenamide (CBS, Rhenogran® CBS-800 purchased from RheinChemie, Germany), 2 phr of diphenylguanidine (SDPG, Rhenogran® DPG-80, purchased from RheinChemie, Germany) and 2.2 phr of sulphur (Rhenogran® IS 60-75, purchased from RheinChemie, Germany).

Rubber compositions with different amounts of Rosin as indicated in Table 1 were prepared by mixing in a lab-scale Bra-bender type internal mixer (Haake® Rheomix OX & Polylab® OS from Thermo Scientific® Mixer) using a four step mixing protocol. In the first step, the rubbers SBR and BR were introduced to the mixer and heated. After 0.5 minutes, 50.5 phr of silica, 6.7 phr of the organosilane were added to the rubber. The mixture was mixed for 1 minute and further 50.5 phr of silica, the Rosin-containing material (1.3 phr), 3.7-4.61 phr of the mineral oil (TDAE, E) antioxidant in (Vulkox® 10X 304020) 0.25 phr of antioxidant in (Antilux® 654), 2 phr of 6PPD, 3.2 phr of Zinc Oxide were added to the mixture. After 2.52 phr of stearic acid, the mixture was mixed for a further 1.5 minutes to allow the mixture to reach a temperature of 150 °C. The ram was introduced to the mixture and the mixture was mixed further 5 minutes.
then raised to allow for cleaning and then lowered. When the temperature reached 160°C the mixture was dumped out of the mixer and allowed to cool at room temperature, to provide a first non-productive rubber mixture (STAGE 1 rubber).

In the second step, the STAGE 1 rubber was brought back into the mixer and was set to 80 RPM. After 2 minutes the ram was raised and then lowered. When the temperature of 160°C was reached, the mixture was dumped out of the mixer and allowed to cool at room temperature, to provide a second non-productive rubber mixture (STAGE 2 rubber).

In the third step, the STAGE 2 rubber was brought back into the mixer and the rotor was set to 500 RPM. The vulcanization package 6.2 phr (Rhenogran CBS-80 2 phr, Rhenogran DPG-80 2 phr, Rhenogran IS 60-75 2.2 phr) was added to the mixture. When the temperature of 160°C was reached, the mixture was dumped out of the mixer and allowed to cool at room temperature, to provide a final productive rubber mixture (FINAL STAGE).

The final productive mixtures were cured at 160°C for 15 minutes and then used for physical, dynamic, and tensile mechanical tests.

Performance of rubber compositions

As explained in more detail below, rubber compositions of examples 1-4 at different stages of production, or were tested for different properties including Mooney viscosity, tensile mechanical properties, hardness, and rebound properties, etc.

Mooney viscosity

The large rotor Mooney viscosity of the rubber compositions of examples 1-10 was determined at STAGE CL according to procedures described in ASTM D-1646-89 (ISO 289). The test was performed using a large rotor at 100°C. The sample was preheated at the test temperature for 10 min before the rotor started to rotate at 35 rpm, and then the Mooney viscosity (ML (1+4) at 100°C) was recorded as the torque after the rotor had rotated for 4 min at 2 rpm (aver-
As it can be seen in Table 2a the Mooney viscosity (ML\((1+4)\) at \(100^\circ\text{C}\)) of the uncured rubber mixtures comprising rosin (STAGE \(G1\)) rubber of examples 2 and in which are greatly diminished when compared to the uncured mixtures of rubber compositions in which do not comprise rosin (examples 1 and 3).

The reduction of the viscosity at \(100^\circ\text{C}\) means that the production of products derived from rubber compositions comprising both rosin acid and an organosilane can be significantly improved.

In particular, the lower ML\((1+4)\) at \(100^\circ\text{C}\) in the non-productive stocks (STAGE \(G1\)) will facilitate the better rubber processing including ease for handling and the continuation of the mixing process which will greatly increase the plant productivity and the production throughput.

The viscosity of the final productive rubber mixtures was characterized by measuring torque before and during the curing process \(160^\circ\text{C}\). This was conducted by recording the minimum torque using a Prescott Rheo-Line Moving Die Rheometer for monitoring the curing process according to the ISO 5602/25 or ASTM D5289 procedure. The testing conditions used were a frequency of 0.67 Hz and a strain of 0.7% at \(160^\circ\text{C}\).
Table 2b sets forth the cure rate properties as determined using a moving die rheometer at 160°C for 17 minutes of Examples 1-4 for the FINAL STAGE.

<table>
<thead>
<tr>
<th></th>
<th>Example 1</th>
<th>Example 2</th>
<th>Example 3</th>
<th>Example 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDR @160°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M_D (dNm)</td>
<td>2.84</td>
<td>2.61</td>
<td>2.71</td>
<td>2.76</td>
</tr>
<tr>
<td>M_H (dNm)</td>
<td>17.68</td>
<td>17.40</td>
<td>17.20</td>
<td>17.99</td>
</tr>
<tr>
<td>M_H-M_D (dNm)</td>
<td>14.84</td>
<td>14.79</td>
<td>14.49</td>
<td>15.23</td>
</tr>
<tr>
<td>TC90% (min.)</td>
<td>10.10</td>
<td>9.71</td>
<td>8.12</td>
<td>7.99</td>
</tr>
</tbody>
</table>

Table 3a sets forth the tensile mechanical properties of the Examples 1-4 after the FINAL STAGE. The tensile mechanical properties of the rubber can be measured using standard procedures such as those described in ASTM D746-10 for uncured rubber and ISO 37 for cured rubber. Parameters commonly used in the art which may be measured include the tensile strength measured at 50% elongation (M50), 200% elongation (M200), and at 300% elongation (M300). The M300/M100 ratio gives an idea of the reinforcement properties of the rubber composition. On.

<table>
<thead>
<tr>
<th></th>
<th>Example 1</th>
<th>Example 2</th>
<th>Example 3</th>
<th>Example 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M50 (MPa)</td>
<td>1.25</td>
<td>1.27</td>
<td>1.30</td>
<td>1.43</td>
</tr>
<tr>
<td>M100 (MPa)</td>
<td>2.02</td>
<td>2.03</td>
<td>2.26</td>
<td>2.45</td>
</tr>
<tr>
<td>M200 (MPa)</td>
<td>4.97</td>
<td>4.91</td>
<td>6.25</td>
<td>6.42</td>
</tr>
<tr>
<td>M300 (MPa)</td>
<td>9.61</td>
<td>9.28</td>
<td>12.64</td>
<td>12.18</td>
</tr>
<tr>
<td>M300/M100</td>
<td>4.75</td>
<td>4.57</td>
<td>5.61</td>
<td>4.96</td>
</tr>
<tr>
<td>EB (%)</td>
<td>421.44</td>
<td>492.41</td>
<td>403.27</td>
<td>399.89</td>
</tr>
<tr>
<td>Tb (MPa)</td>
<td>15.83</td>
<td>17.97</td>
<td>19.73</td>
<td>18.28</td>
</tr>
</tbody>
</table>
using a Wallace Shore A tester. Rebound Resilience was measured according to ISO 4662 at 22 °C and 60 °C using a Zwick/Roell rebound tester.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Example 1</th>
<th>Example 2</th>
<th>Example 3</th>
<th>Example 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rebound Resilience (%)</td>
<td>36.26</td>
<td>35.37</td>
<td>36.85</td>
<td>35.40</td>
</tr>
<tr>
<td>Hardness Shore A</td>
<td>64.8</td>
<td>64</td>
<td>62.5</td>
<td>63.8</td>
</tr>
</tbody>
</table>

Table 2b,2c indicates that the rosins containing compounds do not negatively impact the physical properties of the cured compound whilst improving the viscosity. Therefore, the processing of the compound is facilitated.

The compositions and methods of the appended claims are not limited in scope by the specific compositions and methods described herein, in which are intended as illustrations of a few aspects of the claims. Any compositions and methods that are functionally equivalent are intended to fall within the scope of the appended claims. Furthermore, while only certain representative compositions and methods disclosed herein are specifically described, other combinations of the compositions and methods also are intended to fall within the scope of the appended claims, even if not specifically recited. Thus, a combination of steps, elements, components, or constituents may be explicitly mentioned herein or elsewhere, or other combinations of steps, elements, components, and constituents are included, even though not explicitly stated.
It may be evident to those of ordinary skill in the art, upon review of the exemplary embodiments herein, that further modifications, equivalents, and variations are possible. All parts and percentages in the examples, as well as in the remainder of the specification, are by weight unless otherwise specified. Further, any range of numbers recited in the specification for claims, such as representing a particular set of properties, units of measure, reconditions, or states, or percentages, is intended to literally incorporate expressly by reference or otherwise, any number falling within such range, including any subset thereof as recited. For example, whenever a numerical range with a lower limit, \( R_L \), and an upper limit, \( R_U \), is disclosed, any number \( R \) falling within the range is specifically disclosed. In particular, the following numbers within the range are specifically disclosed: \( R = R_L + k(R_U - R_L) \), where \( k \) is a variable ranging from 1% to 100% (with \( 1\% \) increments, e.g., \( k = 1\%, 2\%, 3\%, 4\%, 5\%, \ldots \), 50%, 51%, 52%, 95%, 96%, 97%, 98%, 99%, or 100%). Moreover, any numerical range represented by any two values of \( R \), such as calculated above, is also specifically disclosed. Any modifications of the invention, or in addition to those shown and described herein, will become apparent to those skilled in the art from the foregoing description and accompanying drawings. Such modifications are intended to fall within the scope of the appended claims. All publications cited herein are incorporated by reference in their entirety.

The terms "comprising" and variations thereof as used herein, is used synonymously with the terms "including" and variations thereof, are open, non-limiting terms. Although the terms "comprising" and "including" have been used herein to describe various embodiments, the terms "consisting essentially of" and "consisting of" can be used in place of "comprising" and "including".
ing" to provide for more specific embodiments of the invention and are also disclosed. Other than where noted, all numbers expressing geometries, dimensions, etc. and so forth used in the specification and claims are to be understood at the very least, and not as an attempt to limit the scope of the claims, but to be construed in light of the number of significant digits and of ordinary rounding approaches.

Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of skill in the art to which the disclosed invention belongs. Publications cited herein and the materials for which they are cited are specifically incorporated by reference.

The preceding example and figures are meant only as illustrations; the following claims define the inventive subject matter.
1. A rubber composition comprising:
   (A) a rubber;
   (B) silica;
   (C) an organosilane having at least one hydroxy, cyclic and/or bridged alkoxy group;
   (D) a rosin-containing material comprising at least one rosin compound and derivatives thereof, selected from at least one of rosin, dimerized rosin, hydrogenated rosin, disproportionated rosin, decarboxylated rosin, and rosin ester.

2. The composition of claim 1, wherein the rosin-containing material has an acid number of 0.5 to 190 mg KOH/g, in particular from 1 to 185 mg KOH/g, more in particular from 1.5 to 180 mg KOH/g, yet more in particular from 2 to 175 mg KOH/g; and/or has a softening point from 40 to 170 °C, in particular from 45 to 160 °C, more in particular from 50 to 150 °C, yet more in particular from 55 to 145 °C.

3. The rubber composition of claim 1, or 2, wherein the rosin-containing material is a rosin or derivative thereof, in particular selected from tall oil rosin, gum rosin, and wood rosin, and more in particular the rosin-containing material is tall oil rosin.

4. The rubber composition of any one of claims 1 to 3, wherein the organosilane has at least one mercapto and/or silanol functional groups.

5. The rubber composition of any one of claims 1 to 4, wherein the organosilane has both blocked and unblocked mercapto groups.

6. The rubber composition of any one of claims 1 to 5, wherein the cyclic and/or bridged alkoxy groups are derived from diols.
7. The rubber composition of any one of claims 1 to 6, wherein the blocking group comprises a carbonyl group.

8. The rubber composition of claim 7, wherein the blocking group is of formula -COR', wherein R' is an unsubstituted, or substituted, branched, linear, mono-, di-, tri- or tetraalkyl, aralkyl, alkenyl, alkynyl, or aryl group having at least 1 carbon atom, and in particular at least 3 carbon atoms, and more in particular at least 5 carbon atoms, and more in particular at least 7 atoms.

9. The rubber composition of any one of claims 1 to 8, wherein the blocking group is an octanoyl group.

10. The rubber composition of any one of claims 1 to 9, wherein the organosilane is an organosilane of formula (I):

\[
\text{(I)}
\]

20. \( R^1 \) is a hydrocarbon radical containing from 4 to 10 carbon atoms, preferably an alkyl radical, and preferably containing 7 to 9 carbon atoms; wherein \( R^2 \) is an alkenylene radical containing from 3 to 6 carbon atoms, preferably 4 carbon atoms; wherein \( R^3 \) is an alkenylene radical containing from 3 to 8 carbon atoms, preferably 4 carbon atoms; wherein \( R^4 \) radicals are the same or different alkyl radicals containing from 3 to 80 carbon atoms; wherein \( R^5 \) radicals are the same or different alkyl radicals containing from 3 to 80 carbon atoms;
(A) The same or different alkyl radicals containing from 3 to 8 carbon atoms, or
(B) Combined to form an individual alkyl radical, all having if from 3 to 8 carbon atoms; as;
wherein p is a value within the range of from 3 to 6;
wherein q is the total % of C and aromatic is at least 15, which may be, for example, from 0 to about 15 or more; and
wherein s and u are each values within a range of from 0 to 0.8.

11.1 The rubber composition of claim 10, 1 wherein p is
wherein p is a value within the range of from 3 to 6;
wherein q is the total % of C and aromatic is at least 15, which may be, for example, from 0 to about 15 or more; and
wherein s and u are each values within a range of from 0 to 0.8.

12.1 The rubber composition of claim any one of claims 13 to 11, 1 wherein s is
20 the organosilane is a monomer, dimer or oligomer.

13.1 The rubber composition of claim any one of claims 13 to 12, 1 wherein s is
the organosilane is an oligomer.

25.14.1 The rubber composition of claim any one of claims 13 to 11, 1 wherein s is
the rubber (A) (A) is selected from at least one of styrene/butadiene copolymer, (SBR) BR, polybutadiene (BR) BR, natural rubber, polyisoprene, neoprene, isobutylene propylene copolymer (IR) BR, styrene/isoprene/butadiene interpolymer (SIBR) BR, and isoprene/styrene 30copolymer.

15.1 The rubber composition of claim any one of claims 13 to 14, 1 wherein s is
the amount of the organosilane in (c) (cis) is from 0.05 to 75 phr, wherein in particular is from 0.1 to 60 phr, more in particular is from 0.5 to 50 35 phr, more in particular is from 1 to 30 phr, more in particular is...
lar]{from:0 to 15 phr} wherein phr is the weight parts of organosilane per 100 weight parts of rubber component \( \text{A} \).

16.1. The rubber composition of any one of claims 1 to 15, wherein the amount of rosino-containing material \( \text{D} \) (E is from:0.001 to 75 phr, hrin i particular {from:0.01 to 5 phr, hrin i particular {from:0.1 to 2.5 phr, hmore} in particular {from:0.01 to 0.5 phr} to 5.05 phr} wherein phr is the weight parts of rosino-containing material \( \text{D} \) per 100 weight parts of rubber component \( \text{A} \).}

17.1. The rubber composition of any one of claims 1 to 16, wherein the amount of silica \( \text{B} \) (E is from:0.5 to 150 phr, hrin i particular {from:2.5 to 130 phr, hrin i particular {from:40 to 6515.15 phr} wherein phr is the weight parts of silica \( \text{B} \) per 100 weight parts of rubber component \( \text{A} \).}

18.1. The rubber composition of any one of claims 1 to 17 comprising is from 5-150 phr of silica \( \text{B} \) (E is from:0.05-75 phr of the organosilane \( \text{C} \) \{C 20 and \( \text{D} \) wherein phr is the weight parts of each \( \text{C} \) \{C \{Cor o \} \{Iper \}er 100 weight parts of rubber component \( \text{A} \).}

19.1. The rubber composition of any one of claims 1 to 18, having, ng, 25 when the rubber composition is in STAGE1G1, la Mooney viscosity from:0.1 to 75 7% lower, erin i particular {from:2.1 to 60 6% lower, emore} re in i particular {from:3.1 to 50 5% lower, eeven more} in i particular {from:om 4 to 4 4% lower} than the Mooney viscosity of ca similar rubber composition \( \text{A} \) or a similar \( \text{A} \) similar rubber composition \( \text{A} \) with rosin-containing material.}

30

20.20A tire comprising \( \text{A} \) the rubber composition of any one of claims 1 to 19.19.

21.2. Use of ca rosin-containing material \( \text{D} \) selected: from:rosin, iindii- 35 merized:rocin, in, hydrogenated :rocin, in, disproportionated :rocin, in, deoxygenated :rocin, and rosin ester (component \( \text{D} \) D)
in a rubber composition further comprising a rubber (component A); silica (component B); and an organosilane having at least one hydroxy, cyclic and/or bridged alkoxy group; to obtain a rubber composition having, when the rubber composition is not cured, a reduced Mooney viscosity when compared to a similar uncured rubber composition without component D. D.

22. A method for preparing a rubber composition according to any one of the claims to comprising: mixing:
   (A) a rubber; and
   (B) silica;
   (C) and/or an organosilane having at least one hydroxy, cyclic and/or bridged alkoxy group; and
   (D) a rosin-containing material selected from rosin, dimerized rosin, hydrogenated rosin, disproportionated rosin, decarboxylated rosin, and rosin ester.
A. CLASSIFICATION

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B. FIELDS SEARCHED

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of box C. See patent family annex.

Date of the actual completion of the international search:
2 March 2016

Date of mailing of the international search report:
11/03/2016

Name and mailing address of the IAI:

European Patent Office, P.B. 1018 Patentclass 2 NL-2280 HU Rijswijk
Tel. (+31-70) 340-2045, Fax. (+31-70) 340-3016

Authorized officer:
Russel 1, Graham
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