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(54) Title: **CROSSLINKED POLYSULFIDE-CONTAINING CYCLOALIPHATIC COMPOUND**(57) Abstract: A crosslinked polysulfide-containing cycloaliphatic compound, useful as a crosslinker for filled sulfur-vulcaniz-  
able elastomer compositions, is represented by the general formula:  $[(C_aH_{2a})_mG^1(-C_bH_{2b}S_x)_{n-m} \text{ and } C_eH_{2e}-G^2-C_dH_{2d}S_y]_p[R]_q$   
wherein  $G^1$  is a saturated, monocyclic aliphatic group of valence  $n$  containing from 5 to 12 carbon atoms and optionally contain-  
ing at least one halogen or a saturated monocyclic silicone  $[RSiO-]_n[R_2SiO-]_r$  group of valence  $n$ ;  $G^2$  is a saturated, divalent cyclic  
aliphatic group of valence 2 containing from 5 to 12 carbon atoms and optionally containing at least one halogen or a saturated  
monocyclic silicone  $[RSiO-]_n[R_2SiO-]_r$  group of valence  $n$ ; each  $R$  independently is a selected from the group consisting of a hy-  
drogen atom, monovalent hydrocarbon of up to 20 carbon atoms and a halogen atom; each occurrence of subscripts  $a, b, c, d, m,$   
 $n, o, p, q, x$  and  $y$  independently is an integer wherein  $a$  is 2 to 6;  $b$  is 2 to 6;  $c$  is 1 to 6;  $d$  is 1 to 6;  $m$  is 1 or 2;  $n$  is 3 to 5;  $o$  is a  
positive integer,  $p$  is 0 or a positive integer;  $q$  is a positive integer;  $r$  is an integer of from 0 to 3;  $x$  is 1 to 10 and  $y$  is 1 to 10, with  
the provisos that, (i) at least one  $x$  is 2 to 10; (ii) the ratio of  $p$  to  $o$  is less than 1 to 5; and  $q$  is equal to the sum of unfilled va-  
lences of the  $(C_aH_{2a})_mG^1(-C_bH_{2b}S_x)_{n-m}$  and  $C_eH_{2e}-G^2-C_dH_{2d}S_y$  groups.

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**CROSSLINKED POLYSULFIDE-CONTAINING CYCLOALIPHATIC COMPOUND,  
PROCESS FOR ITS PREPARATION, FILLED SULFUR-VULCANIZABLE  
ELASTOMER COMPOSITION CONTAINING SAME AND  
ARTICLES FABRICATED THEREFROM**

**FIELD OF THE INVENTION**

**[0001]** The present invention relates to organosulfur compounds, processes for their preparation, filled sulfur-vulcanizable compositions containing organosulfur compounds as crosslinkers (vulcanizing agents) and articles such as tires, tire tread, weather stripping, hose, belts, seals, gaskets, shoe soles, and the like, fabricated from such compositions.

**DESCRIPTION OF THE RELATED ART**

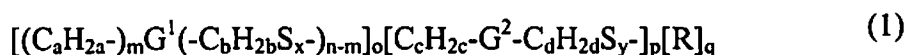
**[0002]** Elemental sulfur is commonly used as a vulcanizing agent for unsaturated diene elastomers (rubbers). The crosslinks formed with sulfur are primarily polysulfidic crosslinks that increase the thermal stability of the elastomer vulcanizates.

**[0003]** The use of organic compounds possessing sulfur-containing reactive groups as vulcanizing agents for diene rubbers is known. These organosulfur compounds often contain only two dithiocarbamate or thiosulfonate groups chemically bonded to a bridging group. The low number of tie points provided by such compounds results in inadequate crosslinking of diene rubbers thus failing to achieve vulcanizates exhibiting a satisfactory balance of wear, traction and rolling resistance. In instances where more than two dithiocarbamate or thiosulfonate groups are chemically bonded to a bridging group, the bridging group often contains unstable linkages such as ether or ester linkages or lacks the flexibility needed to dissipate energy that can propagate cracks when a crosslinked (cured) elastomer is subjected to mechanical stress. When these vulcanizing agents are curing the diene rubber, they generate byproducts, such as amines and thiosulfonic acids, that affect cure rates, corrosion of steel belts, and physical properties of the cure elastomer.

[0004] It would be desirable to have a crosslinker for sulfur-vulcanizable elastomers that improves the wear properties of articles manufactured therefrom, e.g., weather stripping, hose, belts, seals, gaskets, shoe soles, tires and tire components, specifically, tear and abrasive wear, while maintaining hardness, lower tan delta values at temperatures above 40°C and increased tan delta values at temperatures of from 5°C to -15°C, without generating during the curing reaction, undesirable byproducts.

### SUMMARY OF THE INVENTION

[0005] According to the invention, there is provided a crosslinked polysulfide-containing cycloaliphatic compound, and mixtures thereof, of the general formula:



wherein  $G^1$  is a saturated, monocyclic aliphatic group of valence  $n$  containing from 5 to 12 carbon atoms and optionally containing at least one halogen or a saturated monocyclic silicone  $[RSiO-]_n[R_2SiO-]_r$  group of valence  $n$ ;  $G^2$  is a saturated, divalent cyclic aliphatic group of valence 2 containing from 5 to 12 carbon atoms and optionally containing at least one halogen or a saturated monocyclic silicone  $[RSiO-]_n[R_2SiO-]_r$  group of valence  $n$ ; each  $R$  independently is a selected from the group consisting of a hydrogen atom, monovalent hydrocarbon of up to 20 carbon atoms and a halogen atom; each occurrence of subscripts  $a, b, c, d, m, n, o, p, q, x$  and  $y$  independently is an integer wherein  $a$  is 2 to 6;  $b$  is 2 to 6;  $c$  is 1 to 6;  $d$  is 1 to 6;  $m$  is 1 or 2;  $n$  is 3 to 5;  $o$  is a positive integer,  $p$  is 0 or a positive integer;  $q$  is a positive integer;  $r$  is an integer of from 0 to 3;  $x$  is 1 to 10 and  $y$  is 1 to 10, with the provisos that,

- (i) at least one  $x$  is 2 to 10;
- (ii) the ratio of  $p$  to  $o$  is less than 1 to 5; and
- (iii)  $q$  is equal to the sum of unfilled valences of the  $(C_aH_{2a})_mG^1(-C_bH_{2b}S_x-)_{n-m}$  and  $C_cH_{2c}-G^2-C_dH_{2d}S_y-$  groups.

[0006] Further, in accordance with the present invention, the foregoing crosslinked polysulfide-containing cycloaliphatic compound is prepared by the process which comprises:

- a) reacting poly-alkenyl-substituted cycloalkane with thioacid in the presence of a free-radical source to provide poly-thiocarboxylate-substituted alkylcycloalkane;
- b) reacting poly-thiocarboxylate-substituted alkylcycloalkane with deblocking agent to form free poly-mercaptan-functional alkylcycloalkane;
- c) reacting free poly-mercaptan-functional alkylcycloalkane with an oxidizing agent selected from halogenated sulfur-containing compound represented by the general formula:

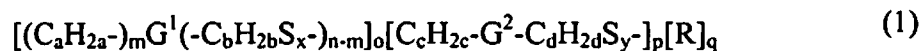


wherein  $X^1$  is chlorine, bromine or iodine atom,  $X^2$  is  $X^1$ , hydrogen or a hydrocarbon of up to 12 carbon atoms, and  $z$  independently an integer wherein  $z$  is 1 to 10; peroxides; hydroperoxides; and oxygen,

to provide crosslinked polysulfide-containing cycloaliphatic compound.

[0007] According to another aspect of the present invention, a curable filled elastomer composition is provided which comprises:

- (i) at least one sulfur-vulcanizable elastomer;
- (ii) at least one particulate filler; and,
- (iii) a crosslinking effective amount of, as crosslinker for sulfur-vulcanizable elastomer (i), at least one crosslinked polysulfide-containing cycloaliphatic compound of the general formula:



wherein  $G^1$  is a saturated, monocyclic aliphatic group of valence  $n$  containing from 5 to 12 carbon atoms and optionally containing at least one halogen or a saturated monocyclic

silicone  $[\text{RSiO-}]_n[\text{R}_2\text{SiO-}]_r$  group of valence  $n$ ;  $\text{G}^2$  is a saturated, divalent cyclic aliphatic group of valence 2 containing from 5 to 12 carbon atoms and optionally containing at least one halogen or a saturated monocyclic silicone  $[\text{RSiO-}]_n[\text{R}_2\text{SiO-}]_r$  group of valence  $n$ ; each R independently is a selected from the group consisting of a hydrogen atom, monovalent hydrocarbon of up to 20 carbon atoms and a halogen atom; each occurrence of subscripts a, b, c, d, m, n, o, p, q, x and y independently is an integer wherein a is 2 to 6; b is 2 to 6; c is 1 to 6; d is 1 to 6; m is 1 to 2; n is 3 to 5; o is a positive integer, p is 0 or a positive integer; q is a positive integer; r is an integer of from 0 to 3; x is 1 to 10 and y is 1 to 10, with the provisos that,

- (i) at least one x is 2 to 10;
- (ii) the ratio of p to o is less than 1 to 5; and
- (iii) q is equal to the sum of unfilled valences of the  $(\text{C}_a\text{H}_{2a-})_m\text{G}^1(-\text{C}_b\text{H}_{2b}\text{S}_x-)_{n-m}$  and  $\text{C}_c\text{H}_{2c}-\text{G}^2-\text{C}_d\text{H}_{2d}\text{S}_y-$  groups.

[0008] According to still another aspect of the present invention, an article such as a tire or tire component such as tread, hose, belt, seal, gasket, and the like, is fabricated by molding a quantity of the foregoing curable filled elastomer composition into the shape of the desired article and thereafter curing the composition.

[0009] In the specification and claims herein, the following terms and expressions are to be understood as indicated.

[0010] The term "elastomer" is synonymous, and therefore interchangeable, with "rubber".

[0011] The expression "coupling agent" means an agent capable of establishing an effective chemical and/or physical bond between a vulcanizable elastomer and its filler. Effective coupling agents have functional groups capable of bonding physically and/or chemically with filler, for example, between a silicon atom of the coupling agent and the hydroxyl (OH) surface groups of the filler to form a surface-O-Si bond, e.g., a siloxane when the surface contains silanols as in the case of silica, and, for example, sulfur atoms

which are capable of bonding physically and/or chemically with the elastomer as a result of vulcanization (curing).

**[0012]** The expression "filler" means a substance that is added to the elastomer to either extend the elastomer or to reinforce the elastomeric network. Reinforcing fillers are materials whose moduli are higher than the organic polymer of the elastomeric composition and are capable of absorbing stress from the organic polymer when the elastomer is strained. Fillers include fibers, particulates, and sheet-like structures and can be composed of inorganic materials such as silicates, silica, clays, ceramics, carbon, diatomaceous earth and organic materials such as organic polymers. The filler can be essentially inert to the other rubber ingredients with which it is admixed or it can be reactive therewith.

**[0013]** The expression "particulate filler" means a particle or grouping of particles that form aggregates or agglomerates. Particulate fillers that are useful herein can be essentially inert to coupling agents with which they are admixed, e.g., silane coupling agents, or they can be reactive therewith.

**[0014]** The term "carrier" means a porous polymer or high surface area filler that has a high adsorption or absorption capability and is capable of carrying up to 75 percent liquid ingredients that may be used in the rubber compounds while maintaining its free-flowing and dry properties. Useful carriers herein are essentially inert to the liquid ingredients and are capable of releasing or deabsorbing liquids when added to the sulfur-vulcanizable elastomeric composition.

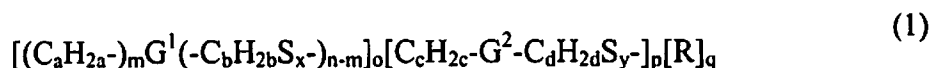
**[0015]** Other than in the working examples or where otherwise indicated, all numbers expressing amounts of materials, reaction conditions, time durations, quantified properties of materials, and so forth, stated in the specification and claims are to be understood as being modified in all instances by the term "about."

**[0016]** It will be understood that any numerical range recited herein includes all sub-ranges within that range and any combination of the various endpoints of such ranges or subranges.

[0017] It will be further understood that any compound, material or substance which is expressly or implicitly disclosed in the specification and/or recited in a claim as belonging to a group of structurally, compositionally and/or functionally related compounds, materials or substances includes individual representatives of the group and all combinations thereof.

### DETAILED DESCRIPTION OF THE INVENTION

[0018] The crosslinked polysulfide-containing cycloaliphatic compound of the invention is represented by the following general formula:



wherein  $G^1$  is a saturated, monocyclic aliphatic group of valence  $n$  containing from 5 to 12 carbon atoms and optionally containing at least one halogen or a saturated monocyclic silicone  $[RSiO-]_n[R_2SiO-]_r$  group of valence  $n$ ;  $G^2$  is a saturated, divalent cyclic aliphatic group of valence 2 containing from 5 to 12 carbon atoms and optionally containing at least one halogen or a saturated monocyclic silicone  $[RSiO-]_n[R_2SiO-]_r$  group of valence  $n$ ; each  $R$  independently is a selected from the group consisting of a hydrogen atom, monovalent hydrocarbon of up to 20 carbon atoms and a halogen atom; each occurrence of subscripts  $a, b, c, d, m, n, o, p, q, x$  and  $y$  independently is an integer wherein  $a$  is 2 to 6;  $b$  is 2 to 6;  $c$  is 1 to 6;  $d$  is 1 to 6;  $m$  is 1 to 2;  $n$  is 3 to 5;  $o$  is a positive integer,  $p$  is 0 or a positive integer;  $q$  is a positive integer;  $r$  is an integer of from 0 to 3;  $x$  is 1 to 10 and  $y$  is 1 to 10, with the provisos that,

- (i) at least one  $x$  is 2 to 10;
- (ii) the ratio of  $p$  to  $o$  is less than 1 to 5; and
- (iii)  $q$  is equal to the sum of unfilled valences of the  $(C_aH_{2a})_m G^1 (-C_bH_{2b}S_x)_{n-m}$  and  $C_cH_{2c}-G^2-C_dH_{2d}S_y$  groups.

[0019] The expression "monovalent hydrocarbon group" means any hydrocarbon group from which one hydrogen atom has been removed and is inclusive of alkyl, alkenyl, alkynyl, cyclic alkyl, cyclic alkenyl, cyclic alkynyl, aryl, aralkyl and arenyl.

[0020] The term "alkyl" means any monovalent, saturated straight, branched or cyclic hydrocarbon group; the term "alkenyl" means any monovalent straight, branched, or cyclic hydrocarbon group containing one or more carbon-carbon double bonds where the site of attachment of the group can be either at a carbon-carbon double bond or elsewhere therein; and, the term "alkynyl" means any monovalent straight, branched, or cyclic hydrocarbon group containing one or more carbon-carbon triple bonds and, optionally, one or more carbon-carbon double bonds, where the site of attachment of the group can be either at a carbon-carbon triple bond, a carbon-carbon double bond or elsewhere therein. Examples of alkyls include methyl, ethyl, propyl and isobutyl. Examples of alkenyls include vinyl, propenyl, allyl, methallyl, ethylidenyl norbornane, ethylidene norbornyl, ethylidenyl norbornene and ethylidene norbornenyl. Examples of alkynyls include acetylenyl, propargyl and methylacetylenyl.

[0021] The expressions "cyclic alkyl", "cyclic alkenyl", and "cyclic alkynyl" include bicyclic, tricyclic and higher cyclic structures as well as the aforementioned cyclic structures further substituted with alkyl, alkenyl, and/or alkynyl groups. Representative examples include norbornyl, norbornenyl, ethylnorbornyl, ethylnorbornenyl, cyclohexyl, ethylcyclohexyl, ethylcyclohexenyl, cyclohexylcyclohexyl and cyclododecatrienyl.

[0022] The term "aryl" means any monovalent aromatic hydrocarbon group; the term "aralkyl" means any alkyl group (as defined herein) in which one or more hydrogen atoms have been substituted by the same number of like and/or different aryl (as defined herein) groups; and, the term "arenyl" means any aryl group (as defined herein) in which one or more hydrogen atoms have been substituted by the same number of like and/or different alkyl groups (as defined herein). Examples of aryls include phenyl and naphthalenyl. Examples of aralkyls include benzyl and phenethyl. Examples of arenyls include tolyl and xylyl.

[0023] Representative non-limiting examples of saturated, monocyclic aliphatic groups  $G^1$  in the crosslinked polysulfide-containing cycloaliphatic compounds of the invention are trivalent, tetravalent and pentavalent cyclopentane, cyclohexane, cycloheptane, cyclooctane, cyclodecane and cyclododecane. It is to be understood that



the attachment of the  $C_aH_{2a}$ - and  $-C_bH_{2b}S_x$ - groups occurs in either an axial or equatorial stereochemical configuration about cycloalkyl ring  $G^1$ . The polysulfide-containing cycloaliphatic compounds herein also include mixtures of stereoisomers in which the positions of the  $C_aH_{2a}$ - and  $-C_bH_{2b}S_x$ - groups in any one stereoisomer can all be in the equatorial position, the axial position or both the equatorial and axial positions. It is preferred that a mixture of stereoisomers herein contain at least 50 weight percent of isomer in which all the  $C_aH_{2a}$ - and  $-C_bH_{2b}S_x$ - groups are in the equatorial position relative to cycloaliphatic group  $G^1$ , and more preferably contain at least 80, and most preferably at least 90, weight percent of said stereoisomer. The stereochemistry about the cycloalkyl ring  $G^1$  is usually determined in the preparation of the poly-alkenyl-substituted cycloalkane intermediate or reactant. For example, in preparing 1,2,4-trivinylcyclohexane from the thermal rearrangement of cis, trans, trans-1,5,9-cyclododecantriene, the reaction conditions can effect the stereochemistry about the cyclohexyl ring. Distillation of the polyalkenyl-substituted cycloalkane or other separation method, such as preparative liquid chromatography can also be used to obtain the desired ratio of stereochemical isomers.

[0024] Representative non-limiting examples of saturated, monocyclic aliphatic groups  $G^2$  in the crosslinked polysulfide-containing cycloaliphatic compound of the invention are divalent cyclopentane, cyclohexane, cycloheptane, cyclooctane, cyclodecane and cyclododecane. It is to be understood that the attachment of the  $C_cH_{2c}$ - and  $-C_dH_{2d}S_y$ - groups occurs in either an axial or equatorial stereochemical configuration about cycloalkyl ring  $G^2$ . The crosslinked polysulfide-containing cycloaliphatic compounds herein also include mixtures of stereoisomers in which the positions of the  $C_cH_{2c}$ - and  $-C_dH_{2d}S_y$ - groups in any one stereoisomer can all be in the equatorial position, the axial position or both the equatorial and axial positions. It is preferred that a mixture of stereoisomers herein contain at least 50 weight percent of isomer in which all the  $C_cH_{2c}$ - and  $-C_dH_{2d}S_y$ - groups are in the equatorial position relative to cycloaliphatic group  $G^2$ , and more preferably contain at least 80, and most preferably at least 90 weight percent of said stereoisomer. The stereochemistry about the cycloalkyl ring  $G^2$  is usually determined in the preparation of the di-alkenyl-substituted cycloalkane intermediate or reactant.

[0025] Representative and non-limiting examples of R in the crosslinked polysulfide-containing cycloaliphatic compound of the invention are hydrogen, methyl, ethyl, propyl, isopropyl, butyl, 2-ethylhexyl, cyclohexyl, cyclopentyl, phenyl, benzyl, tolyl, xylyl, methylbenzyl, chloro, bromo, iodo and the like.

[0026] The divalent linking groups,  $C_aH_{2a}-$ , is bonded to  $G^1$  and the end sulfur from either  $-C_bH_{2b}S_x-$  or  $-C_dH_{2d}S_y-$  group. In this notation, the dash (-) on the carbon of the group,  $-C_bH_{2b}S_x-$ , is defined as a carbon that is filling an unfilled valence of  $G^1$ . In this notation, the dash (-) on the carbon of the group,  $-C_dH_{2d}S_y-$ , is defined as a carbon that is filling an unfilled valence of  $G^2$ . The dash (-) on the sulfur of the group,  $-C_bH_{2b}S_x-$ , is defined as the end sulfur of the chain,  $S_x-$ , that is filling an unfilled valence of  $C_aH_{2a}-$ ,  $C_cH_{2c}-$  or R. The dash (-) on the sulfur of the group,  $-C_dH_{2d}S_y-$ , is defined as the end sulfur of the chain,  $S_y-$ , that is filling an unfilled valence of  $C_aH_{2a}-$ ,  $C_cH_{2c}-$  or R.

[0027] The divalent linking groups,  $C_cH_{2c}-$ , is bonded to  $G^2$  and the end sulfur from either  $-C_bH_{2b}S_x-$  or  $-C_dH_{2d}S_y-$  group. In this notation, the dash (-) on the carbon of the group,  $C_cH_{2c}-$ , is defined as a carbon that is filling an unfilled valence of  $G^2$ .

[0028] The value of q is a positive integer. The proviso requires that q is equal to the sum of unfilled valences of the  $(C_aH_{2a})_mG^1(-C_bH_{2b}S_x-)_{n-m}$  and  $C_cH_{2c}-G^2-C_dH_{2d}S_y-$  groups. It is meant that after all the bonds are formed between  $(C_aH_{2a})_mG^1(-C_bH_{2b}S_x-)_{n-m}$  and  $C_cH_{2c}-G^2-C_dH_{2d}S_y-$ , there are sulfur atoms containing a dash (-), which represents bonding electrons that are looking to form a bond. The number of these sulfur atoms is expressed by the equation:

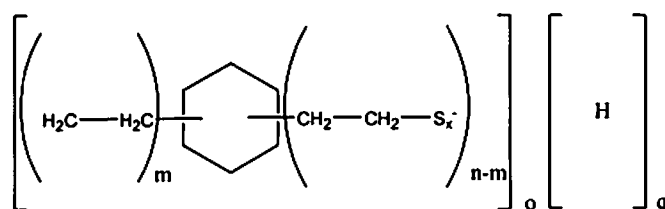
$$q = \Sigma (n-m) - \Sigma m$$

wherein  $\Sigma (n-m)$  is the sum of the independent value of (m-n) for each repeat unit from 1 to o repeat units,  $\Sigma m$  is the sum of the independent value of m for each repeat unit from 1 to o repeat units. It is understood that each repeat unit,  $(C_aH_{2a})_mG^1(-C_bH_{2b}S_x-)_{n-m}$ , may have a different value for m and n. Because q is a positive number,  $\Sigma (n-m)$  is larger than  $\Sigma m$ .

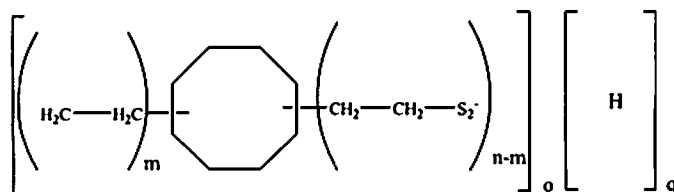
[0029] The crosslinked polysulfide-containing cycloaliphatic compound of the present invention is a crosslinked material, and therefore the value of “o” is large. In one embodiment, the value of o is preferably a positive integer greater than 50, more preferable greater than 100 and most preferably greater than a 1,000. The value of “o” is determined by the particle size of the crosslinked polysulfide-containing cycloaliphatic compound. In another embodiment, the particle size is in the range of 0.1 microns to 10 centimeter, preferably from 10 microns to 1 centimeter, and most preferably from 100 microns to 1 millimeter. Smaller particle size is preferred, because the crosslinked polysulfide-containing cycloaliphatic compound of small particle size is more easily dispersed into the rubber.

[0030] Representative and non-limiting examples of the divalent linking group are methylene, ethylene, propylene, butylene and hexylene. Preferred linking groups are ethylene and propylene.

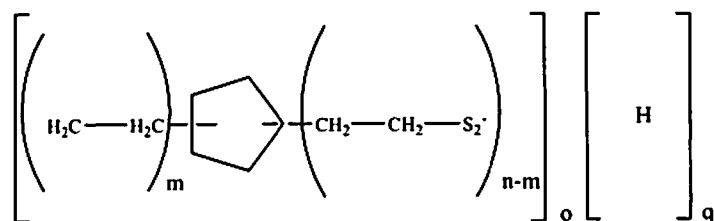
[0031] Representative and non-limiting examples of the sulfur-containing cycloaliphatic compound of the invention include:



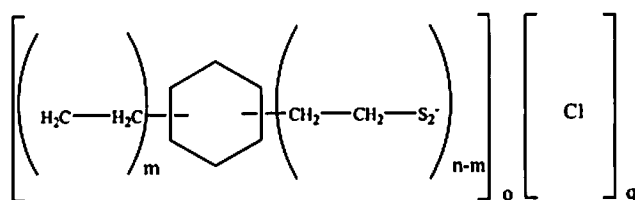
where each m is independently 1 or 2, n is 3, each o and q independently is a positive integer, each x independently an integer from 2 to 6 and the substitution on the ring is 1, 2 and 4;



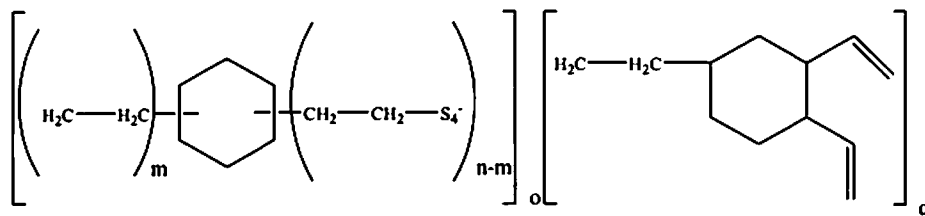
where each m is independently 1 or 2, n is 4, each o and q independently is a positive integer and the substitution on the ring is 1, 3, 5 and 7;



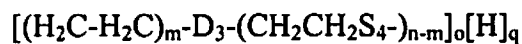
where each  $m$  is independently 1 or 2,  $n$  is 3, each  $o$  and  $q$  independently is a positive integer and the substitution on the ring is 1, 2 and 4;



where each  $m$  is independently 1 or 2,  $n$  is 3, each  $o$  and  $q$  independently is a positive integer and the substitution on the ring is 1, 3 and 5;



where each  $m$  is independently 1 or 2,  $n$  is 3, each  $o$  and  $q$  independently is a positive integer and the substitution on the ring is 1, 2, 4;



where  $D$  represents a  $\text{RSiO-}$  unit, each  $m$  is independently 1 or 2,  $n$  is 3, each  $o$  and  $q$  independently is a positive integer and the substitution on the ring occurs on the silicon atoms, and the like.

**[0032]** Preferred crosslinked polysulfide-containing cycloaliphatic compounds herein include compounds of the formula (1), wherein the  $G^1$  is trivalent cyclohexyl group,  $G^2$  is a divalent vinylcyclohexyl group,  $x$  and  $y$  are 2 to 5, the values of  $a$ ,  $b$ ,  $c$  and  $d$  are 2 or 3.

More preferred is when, on average, 50 percent of the substituents on the cyclohexyl ring are the equatorial position, a, b, c and d are 2, x and y are 3 to 5 and R is hydrogen or a monovalent hydrocarbon of from 1 to 12 carbon atoms.

[0033] The crosslinked polysulfide-containing cycloaliphatic compound of the invention can be prepared by the process which comprises:

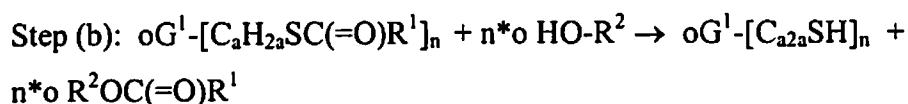
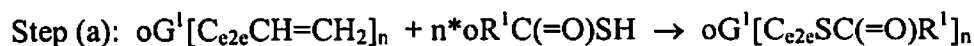
- a) reacting poly-alkenyl-substituted cycloalkane with thioacid in the presence of a free-radical source to provide poly-thiocarboxylate-substituted alkylcycloalkane;
- b) reacting poly-thiocarboxylate-substituted alkylcycloalkane with deblocking agent to form free poly-mercaptan-functional alkylcycloalkane;
- c) reacting the free poly-mercaptan-functional alkylcycloalkane with an oxidizing agent selected from halogenated sulfur-containing compound represented by the general formula:

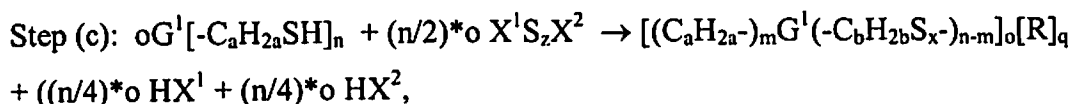


wherein  $X^1$  is chlorine, bromine or iodine atom,  $X^2$  is  $X^1$ , hydrogen or a hydrocarbon of up to 12 carbon atoms, and z independently an integer wherein z is 1 to 10; peroxides; hydroperoxides; and oxygen,

to provide crosslinked polysulfide-containing cycloaliphatic compound.

[0034] The foregoing process for preparing the crosslinked polysulfide-containing cycloaliphatic compound of the invention is illustrated by the chemical equations for reaction steps (a)-(d):





wherein  $G^1$  is a saturated, monocyclic aliphatic group of valence  $n$  containing from 5 to 12 carbon atoms and optionally containing at least one halogen or a saturated monocyclic silicone  $[RSiO-]_n[R_2SiO-]_r$  group of valence  $n$ ; each  $R$  independently is a selected from the group consisting of a hydrogen atom, monovalent hydrocarbon of up to 20 carbon atoms and a halogen atom; each occurrence of subscripts  $a$ ,  $b$ ,  $e$ ,  $m$ ,  $n$ ,  $o$ ,  $q$ , and  $x$  independently is an integer wherein  $a$  is 2 to 6;  $b$  is 2 to 6;  $e$  is 1 to 4;  $m$  is 1 to 2;  $n$  is 3 to 5;  $o$  is a positive integer,  $p$  is 0;  $q$  is a positive integer;  $r$  is an integer of from 0 to 3; and  $x$  is 1 to 10, with the provisos that,

- (i) at least one  $x$  is 2 to 10;
- (ii) the ratio of  $p$  to  $o$  is less than 1 to 5, preferably  $p$  to  $o$  is less than 1 to 20 and more preferably less than 1 to 100 and most preferably the ratio is zero; and
- (iii)  $q$  is equal to the sum of unfilled valences of the  $(C_aH_{2a-})_mG^1(-C_bH_{2b}S_{x-})_{n-m}$  and  $C_eH_{2e}-G^2-C_dH_{2d}S_{y-}$  groups.

[0035] It is understood that for the process above, the value of  $p$  is zero. For crosslinked poly-sulfide cycloaliphatic compounds of formula (1), where  $p$  is a positive integer, the process would involve first making a mixture of  $G^2[-C_{e2e}CH=CH_2]_n$  and  $G^2[-C_{e2e}CH=CH_2]_2$ , and then using this mixture as the reactant in step (a).

[0036] When it is desirable to prepare a polydisulfide, i.e., when  $x$  and  $y$  are 2, the oxidizing agent is a peroxide, hydroperoxide, oxygen, air or mixtures of oxygen with an inert gas.

[0037] The isomeric mixture of the sulfur-containing cycloaliphatic compounds is determined by the stereochemistry of the polyvalent cycloaliphatic compound containing three to five alkenyl groups,  $G[-C_eH_{2e}CH=CH_2]_n$  where  $G$ ,  $e$  and  $n$  are defined above. The stereochemical structure of the reactants is not altered in the addition reaction of the thiocarboxylic acid group in step (a).

[0038] Trivinylcyclohexanes, which are the preferred starting materials for producing the sulfur-containing cycloaliphatic compounds of the present invention, can be formed by pyrolysis of 1,5,9-cyclododecatriene. The conversion of the 1,5,9-cyclododecatriene at elevated temperature, and optionally in the presence of a catalyst, results in the formation of the trivinylcyclohexane compound, as disclosed in U.S. Patent No. 3,011,003 and British Patent No. 848,637, the entire contents of which are incorporated by reference herein.

[0039] The addition reaction of step (a) wherein the thiocarboxylic acid is reacted with a polyvalent cycloaliphatic compound containing three to five alkenyl groups, may optionally be carried out in the presence of a free radical (oxidizing) reagent. Suitable free radical reagents include oxidizing agents that are capable of converting the thiocarboxylic acid to a thiocarboxylic acid radical, i.e.,  $R^1C(=O)S\bullet$ , and include, but are not limited to oxygen, peroxides, hydroperoxides, and the like, and UV radiation.

[0040] In the preparation of the  $G[-C_3H_2SC(=O)R^1]_n$  intermediate, 0.95 to 3 molar equivalents, preferably 1.0 to 1.25 molar equivalents and most preferably a stoichiometric amount of thiocarboxylic acid, is used.

[0041] Effective amounts of peroxide or a hydroperoxide free radical agent can range from 0.01 to 2, and preferably from 0.1 to 0.5, weight percent based upon the weight of the cycloaliphatic compound containing three to five alkenyl groups. When oxygen is used as the free radical generator, the source of the oxygen can be pure oxygen gas, air or a mixture of oxygen and an inert gas. Mixtures of oxygen and inert gas can contain from 3 to 15 weight percent oxygen with the balance being inert gas. Air or mixtures of oxygen and inert gas are generally preferred due to the difficulties in handling pure oxygen in the presence of organic materials and of these, air is preferred. The source of UV radiation can be a mercury lamp equipped with a quartz window.

[0042] Representative and non-limiting examples of cycloaliphatic compounds containing three to five alkenyl groups include 1,2,4-trivinylcyclohexane, 1,2,4-tripropenylcyclohexane, 1, 3,5-trihexenylcyclohexane, 1,3,5,7-tetravinylcyclooctane,

1,3,5,7,9-pentavinylcyclodecane, and mixtures of at least 80 weight percent cis,cis-1,2,4-trivinyl cyclohexane and at least 5 weight percent trans, cis-1,2,4-trivinylcyclohexane.

[0043] Representative and non-limiting examples of thiocarboxylic acids include thioacetic acid, thiopropanoic acid, thiobutanoic acid, thiohexanoic acid, and the like.

[0044] Representative and non-limiting examples of peroxide and hydroperoxide free radical reagents include di(2,4-dichlorobenzoyl) peroxide, tert-butyl peroxyvalerate, dilauroyl peroxide, dibenzoyl peroxide, tert-butyl peroxy-2-ethylhexanoate, 1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, di(tert-butylperoxy)cyclohexane, tert-butyl peroxy-3,5,5-trimethylhexanoate, tert-butyl peroxyacetate, tert-butyl peroxybenzoate, di-tert-amyl peroxide, dicumyl peroxide, di(tert-butylperoxyisopropyl)benzene, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, tert-butyl peroxyacetate, tert-butyl peroxybenzoate, di-tert-amyl peroxide, dicumyl peroxide, di(tert-butylperoxyisopropyl)benzene, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, tert-butyl cumyl peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3, di-tert-butyl peroxide, and the like.

[0045] The addition reaction of step (a) can be carried out using a  $G^1[-C_aH_{2a}SH]_n$  intermediate or a mixture of  $G^1[-C_aH_{2a}SH]_n$  and  $G^2[-C_aH_{2a}SH]_2$ , at sub-ambient temperature, ambient temperature or elevated temperatures, at sub-atmospheric, atmospheric or supra-atmospheric pressure and in the absence or presence of solvent. A suitable temperature range is from 0°C to 200°C and is preferably from 40°C to 150°C. The reaction will ordinarily be run to completion. The time required to achieve this will depend upon the particular reaction conditions employed and whether a catalyst is used. Reaction times of from 5 minutes to 24 hours are usually suitable. Preferably, atmospheric pressure is used. Typical solvents include hydrocarbon solvents, including aromatic and aliphatic solvents, and chlorinated solvents.

[0046] The transesterification reaction of step (b) is effected by contacting the  $G^1[-C_aH_{2a}SC(=O)R^1]_n$  intermediate resulting from step (a) or a mixture of  $G^1[-C_aH_{2a}SH]_n$  and  $G^2[-C_aH_{2a}SH]_2$  with an alcohol, optionally, in the presence of alkaline catalyst. The amount of alcohol can vary from a stoichiometric amount to a large excess. Typically,



from 1 to 20 equivalents of alcohol are used to affect the transesterification.

Alternatively, the acyl group can be removed by saponification in the present of alkali metal hydroxide. Typical alkali catalysts include lithium hydroxide, sodium hydroxide, potassium hydroxide, sodium methoxide, sodium ethoxide, potassium methoxide, potassium ethoxide, and the like.

[0047] The oxidation reaction of step (c) is effected by reacting the poly-mercapto-cycloaliphatic compound  $G^1[-C_aH_{2a}SH]_n$ , resulting from step (b) or a mixture of  $G^1[-C_aH_{2a}SH]_n$  and  $G^2[-C_aH_{2a}SH]_2$ , with an oxidizing agent selected from the group consisting of peroxide, hydroperoxide, air, oxygen, mixtures of air and an inert gas and preferably with an oxidizing agent of the structure  $X^1S_xX^2$  where  $G^1$ ,  $G^2$ ,  $X^1$ ,  $X^2$ ,  $a$  and  $n$  are defined above. The reagent,  $X^1S_xX^2$ , oxidizes the mercaptans to a disulfide and also inserts additional sulfur into the sulfur chain. The oxidation reaction of step (c) can be carried out at sub-ambient temperature, ambient temperature or elevated temperatures, at sub-atmospheric, atmospheric or supra-atmospheric pressure and in the absence or presence of solvent. The temperature of the reaction can range from  $-10^\circ\text{C}$  to  $200^\circ\text{C}$  and is preferably within the range of  $0^\circ\text{C}$  to  $50^\circ\text{C}$ . The reaction will ordinarily be carried out to completion. Reaction times will vary depending upon the reaction conditions utilized. Reaction times of from 5 minutes to 24 hours are generally suitable. Preferably, atmospheric pressure is employed in order to prevent the loss of halogenating reactant. Typical solvents include hydrocarbon solvents, including aromatic and aliphatic solvents, and halogenated solvents, including fluorinated and chlorinated solvents. Perhalogenated solvents, such as carbon tetrachloride are preferred to prevent reaction of the halogenating reactant with the solvent.

[0048] The crosslinked polysulfide-containing cycloaliphatic compound of the invention is particularly useful as a crosslinker for sulfur-vulcanizable elastomers (i). The crosslinked polysulfide-containing cycloaliphatic compound has from 3 to 5 reactive groups, which react during the curing reactions and do not generate any undesirable byproducts. The crosslinked polysulfide-containing cycloaliphatic compound decomposed during the curing reactions to generate monomeric or oligomer species that are effective crosslinkers because the compounds have three to five tie points to a rubber

molecule. Although not wishing to be constrained by theory, it is believed that higher numbers of tie points, such as greater than 6, can result in a localized area in the bulk rubber that is very crowded and cannot effectively transfer stress, or energy to the polymer chains or fillers. This transfer of stress is facilitated by the cycloaliphatic ring structure. The ring controls the average distance between the polysulfide-functional groups directing them outward from the ring. The orientation enables the reactive groups to attach to different polymer chains thereby improving the crosslinking efficiency. In addition, the cycloaliphatic ring is flexible, alternating between boat, chair and twist conformations. Under high stress, the ring is able to change to conformations that offer a pathway for absorbing energy when the rubber compositions are being stressed. In the absence of this property, energy would be directed to bond scission resulting in poor wear and fatigue properties in the cured rubber composition. Linear and branched alkyl groups are not as effective at orienting the polysulfide groups. Aromatic rings are planar and stiff and therefore cannot undergo these conformational changes. The preferred conformation about the cycloaliphatic ring, especially when the ring is a 1,2,4-substituted cyclohexyl group, is the all cis structure. The polysulfide groups of the compound in rubber are at equilibrium and are primarily in the equatorial position since when the conformation changes to the all -axial positions, it is the 1,3-steric interactions that occur. The all cis structure orients the polysulfide groups away from each other, maximizing the average distance between the polysulfide groups.

**[0049]** The concentration of sulfur-vulcanizable elastomer(s) (i) in the curable filled elastomer composition herein can range from 10 to 99, preferably from 50 to 95, and more preferably from 60 to 85, weight percent of the entire weight of the composition.

**[0050]** The concentration of particulate filler (ii) in the curable filled elastomer composition of the invention can range from 0.5 to 90, preferably from 5 to 60, and more preferably from 10 to 50, weight percent of the entire weight of the composition.

**[0051]** The concentration of crosslinked polysulfide-containing cycloaliphatic compound (iii) of the invention in the filled sulfur-vulcanizable elastomer composition

can range from 0.05 to 30, preferably from 0.5 to 10, and more preferably from 2 to 5, weight percent of the entire weight of the composition.

**[0052]** Reinforcing fillers useful in the present invention include fillers in which the silanes are reactive with the surface of the filler. Representative examples of such fillers include, but are not limited to, siliceous fillers, metal oxides such as silica (pyrogenic and/or precipitated), titanium, aluminosilicate and alumina, clays, talc, and the like. The fillers may be provided in the hydrated form. Particulate, precipitated silica is especially useful as filler, particularly when the silica has reactive surface silanols.

**[0053]** The porosity of a filler can be determined, e.g., by the known technique of mercury porosimetry. In accordance with this method, the pores of a filler are penetrated with mercury after a thermal treatment to remove volatiles. Test conditions utilize a 100 mg sample and the removal of volatiles over 2 hours at 105°C and ambient to 2000 bars pressure. Mercury porosimetry may be performed according to the method described by Winslow et al. in ASTM bulletin, p.39 (1959) or according to DIN 66133. For the measurement, a CARLO-ERBA Porosimeter 2000 may be used. The average mercury porosity specific surface area for a silica filler herein should range from 100 to 300 m<sup>2</sup>/g.

**[0054]** The pore size distribution for a preferred silica, alumina or aluminosilicate filler according to such mercury porosity measurement is considered herein to be such that five percent or less of its pores have a diameter of less than 10 nm, 60 to 90 percent of its pores have a diameter of 10 to 100 nm, 10 to 30 percent of its pores have a diameter at 100 to 1,000 nm and 5 to 20 percent of its pores have a diameter of greater than 1,000 nm.

**[0055]** Suitable silica fillers include those having an average particle size, e.g., in the range of from 10 to 50 nm as determined by electron microscopy, although smaller and larger particle sizes are also useful. Various commercially available silicas that are suitable for use herein include, e.g., those from PPG Industries such as HI-SIL 210 and HI-SIL 243, etc.; those from Rhone-Poulenc such as ZEOSIL 1165MP; those from Degussa such as VN2 and VN3, etc., and those from Huber such as HUBERSIL 8745.

[0056] In one embodiment, one or more fillers are combined with silane coupling agent. The filler can be a mixture of siliceous filler such as silica, alumina and/or aluminosilicate and a carbon black reinforcing pigment. Thus, the filler component can be a mixture of from 15 to 95 weight percent of siliceous filler with the balance being carbon black, e.g., one having a CTAB value of from 80 to 150, and can contain from 0.1 to 20 weight percent of a silane coupling agent, including, illustratively, one or more of 3-mercaptopropyltriethoxysilane, bis-(3-triethoxysilylpropyl) tetrasulfide, bis-(3-triethoxysilylpropyl)disulfide, S-thiooctanonic acid, 3-triethoxysilylpropyl ester, and a silylated core polysulfide, the structure of which are disclosed in U.S. published patent applications 2008/0161461 and 2008/0161477, the entire contents of which are incorporated by reference herein. In another embodiment, the weight ratio of siliceous filler to carbon black is at least 3 to 1, preferably at least 10 to 1 and more preferably at least 30 to 1.

[0057] Filler mixtures can contain from 60 to 95 weight percent of silica, alumina and/or aluminosilicate and, correspondingly, from 40 to 5 weight percent carbon black, and from 0.1 to 20 weight percent silane coupling agent, with the proviso that the mixture of the components add up to 100 percent. The siliceous filler and carbon black may be pre-blended or blended together in the manufacture of the vulcanized rubber.

[0058] Sulfur-vulcanizable elastomers (i) herein include conjugated diene homopolymers and copolymers and copolymers of at least one conjugated diene and aromatic vinyl compound. Suitable organic polymers for preparation of rubber compositions are well known in the art and are described in various textbooks including "The Vanderbilt Rubber Handbook," Ohm, R.F., R.T. Vanderbilt Company, Inc., 1990 and in the "Manual for the Rubber Industry," Kemperman, T. and Koch, S. Jr., Bayer AG, Leverkusen, 1993.

[0059] In one embodiment of the present invention, the sulfur-vulcanizable elastomer is solution-prepared styrene-butadiene rubber (SSBR), e.g., one having a styrene content of from 5 to 50, and preferably from 9 to 36, percent. In other embodiments of the present invention, the sulfur-vulcanizable elastomer is selected from the group consisting

of emulsion-prepared styrene-butadiene rubber (ESBR), natural rubber (NR), ethylene-propylene copolymers and terpolymers (EP, EPDM), acrylonitrile-butadiene rubber (NBR), polybutadiene (BR), and the like, and mixtures thereof.

[0060] Suitable conjugated diene elastomers include, but are not limited to, isoprene and 1,3-butadiene and suitable vinyl aromatic elastomers include, but are not limited to, styrene and alpha methyl styrene. Useful polybutadienes include those typically containing about 90 percent by weight of the units in the cis-1,4-butadiene form.

[0061] The sulfur-vulcanizable elastomer (i) may be selected, e.g., from at least one of cis-1,4-polyisoprene rubber (natural and/or synthetic), emulsion polymerization-prepared styrene/butadiene copolymer rubber, organic solution polymerization-prepared styrene/butadiene rubber, 3,4-polyisoprene rubber, isoprene/butadiene rubber, styrene/isoprene/butadiene terpolymer rubber, cis-1,4-polybutadiene, medium vinyl polybutadiene rubber (35-50 percent vinyl), high vinyl polybutadiene rubber (50-75 percent vinyl), styrene/isoprene copolymers, emulsion polymerization-prepared styrene/butadiene/acrylonitrile terpolymer rubber and butadiene/acrylonitrile copolymer rubber. For some applications, an emulsion polymerization-prepared styrene/butadiene (ESBR) having a relatively conventional styrene content of from 20 to 28 percent bound styrene, or an ESBR having a medium to relatively high bound styrene content of from 30 to 45 percent, may be used.

[0062] Emulsion polymerization-prepared styrene/butadiene/acrylonitrile terpolymer rubbers containing from 2 to 40 weight percent bound acrylonitrile in the terpolymer are also contemplated as diene based rubbers for use in this invention.

[0063] The cured, i.e., vulcanized, elastomer composition herein contains a sufficient amount of filler(s) (ii) as to exhibit a reasonably high modulus, as for example a modulus at 100 percent strain of greater than 8 MPa, and high resistance to tear, as for example, a tear strength of greater than 25 N. In one embodiment of the present invention, the combined weight of the filler may be as low as 5 to 100 parts per hundred parts (phr). In another embodiment, the combined weight of the filler is from 25 to 85 phr and at least one precipitated silica is utilized as a filler in another embodiment. The silica may be

characterized as having a BET surface area, as measured using nitrogen gas, from 40 to 600, and preferably from 50 to 300, m<sup>2</sup>/g. The BET method of measuring surface area is described in the *Journal of the American Chemical Society*, Volume 60, page 304 (1930). The silica may also be characterized as having a dibutylphthalate (DBP) absorption value of from 100 to 350, and preferably of from 150 to 300. Further, the silica, as well as the aforesaid alumina and aluminosilicate, may have a CTAB surface area of from 100 to 220. CTAB surface area is the external surface area as determined with cetyl trimethylammonium bromide with a pH of about 9. The method is described in ASTM D 3849.

[0064] In practice, a vulcanized elastomer article is typically prepared by thermomechanically mixing the sulfur-vulcanizable elastomer(s) (i), filler(s) (ii) and crosslinked polysulfide-containing cycloaliphatic crosslinker(s) (iii) in a sequentially step-wise manner to provide a curable elastomer followed by molding and curing the compositions to provide the article. First, for the aforesaid mixing of the sulfur-vulcanizable elastomer(s) and other components, typically exclusive of the crosslinked polysulfide-containing cycloaliphatic crosslinker, sulfur and sulfur vulcanization accelerators (collectively, curing agents), the elastomer (s) and various elastomer compounding ingredients typically are blended in at least one, and often (in the case of silica-filled low rolling resistance tires) two or more, preparatory thermomechanical mixing stage(s) in suitable mixers. Such preparatory mixing is referred to as nonproductive mixing or non-productive mixing steps or stages. Such preparatory mixing usually is conducted at temperatures of from 140°C to 200°C, and for some compositions from 150°C to 170°C. Subsequent to such preparatory mix stages, in a final mixing stage, sometimes referred to as a productive mixing stage, curing agents, and possibly one or more additional ingredients, are mixed with the rubber compound or composition at lower temperatures, e.g., from 50°C to 130°C, in order to prevent or retard premature curing of the sulfur-vulcanizable rubber, sometimes referred to as scorching. The rubber mixture, also referred to as a rubber compound or composition, typically is allowed to cool, sometimes after or during a process of intermediate mill mixing, between the aforesaid various mixing steps, for example, to a temperature of about 50°C or lower. When it is desired to mold and cure a filled curable elastomer composition, the

desired quantity of the composition is introduced into a mold of appropriate configuration and at a temperature of from 130°C to 200°C, vulcanization of the rubber is achieved through reaction with the sulfur-containing groups of the crosslinked polysulfide-containing cycloaliphatic crosslinker herein and any other sources of free sulfur that may be present in the composition.

**[0065]** Thermomechanical mixing refers to the phenomenon whereby under the high shear conditions in a rubber mixer, the shear forces and associated friction occurring as a result of mixing the rubber compound, or some blend of the rubber compound itself and rubber compounding ingredients in the high shear mixer, the temperature autogeneously increases, i.e., it "heats up". Several chemical reactions may occur at various steps in the mixing and curing processes.

**[0066]** One or more other sulfur sources may be used, for example, in the form of elemental sulfur such as, but not limited to, S<sub>8</sub>. A sulfur donor is considered herein to be a sulfur-containing compound which liberates free, or elemental, sulfur at a temperature in the range of from 140°C to 190°C. Such sulfur donors include polysulfide vulcanization accelerators and organosilane polysulfides with at least two connecting sulfur atoms in their polysulfide bridges. The amount of free sulfur source in the curable composition herein can be controlled or adjusted as a matter of choice relatively independently of the addition of the crosslinked polysulfide-containing cycloaliphatic crosslinker.

**[0067]** In one embodiment of the invention, the rubber composition can comprise 100 parts by weight rubber (phr) of at least one sulfur-vulcanizable rubber selected from the group consisting of conjugated diene homopolymers and copolymers, and copolymers of at least one conjugated diene and aromatic vinyl compound, from 5 to 100 phr, and preferably from 25 to 80 phr, of at least one filler, up to 5 phr curing agent, and from 0.05 to 25 phr of at least one crosslinked polysulfide-containing cycloaliphatic compound of the present invention as crosslinker.

**[0068]** In another embodiment, the filler composition can comprise from 1 to 85 weight percent carbon black based on the total weight of the filler composition and from

0.5 to 10 parts by weight of at least one crosslinked polysulfide-containing cycloaliphatic compound of the present invention as crosslinker based on the total weight of the rubber composition.

[0069] The rubber composition can be prepared by first blending rubber, filler and silane coupling agent, or rubber and filler pretreated with all or a portion of the silane coupling agent, if needed, in a first thermomechanical mixing step to a temperature of from 120°C to 200°C for from 2 to 20 minutes. The crosslinked polysulfide-containing cycloaliphatic crosslinker and other curing agent(s), if present, are then added in a subsequent thermomechanical mixing step at a temperature of from 50°C to 100°C for 1 to 30 minutes. The temperature is then increased to from 130°C to 200°C with curing being accomplished in from 5 to 60 minutes.

[0070] In another embodiment of the present invention, the process may also comprise the additional steps of preparing an assembly of a tire or sulfur-vulcanizable rubber with a tread comprised of the rubber composition prepared according to this invention and vulcanizing the assembly at a temperature in the range of from 130°C to 200°C.

[0071] Other optional ingredients may be added in the rubber compositions of the present invention including coupling agents, e.g., silane coupling agents, curing aids, e.g., sulfur compounds, including activators, retarders and accelerators, processing additives such as oils, plasticizers, tackifying resins, silicas, other fillers, pigments, fatty acids, zinc oxide, waxes, antioxidants and antiozonants, peptizing agents, reinforcing materials such as, for example, carbon black, and so forth. Such additives are selected based upon the intended use and on the sulfur vulcanizable material selected for use, and such selection is within the knowledge of one of skill in the art, as are the required amounts of such additives known to one of skill in the art.

[0072] The vulcanization may be conducted in the presence of additional sulfur vulcanizing agents. Examples of suitable sulfur vulcanizing agents include, for example elemental sulfur (free sulfur) or sulfur-donating vulcanizing agents, for example, an amino disulfide, polymeric polysulfide or sulfur olefin adducts which are conventionally



added in the final, productive, rubber composition mixing step. The sulfur vulcanizing agents, which are common in the art are used, or added in the productive mixing stage, in an amount ranging from 0.4 to 3 phr, or even in some circumstances up to 8 phr, with a range of from 1.5 to 2.5 phr in one embodiment and from 2 to 2.5 phr in another embodiment.

[0073] Vulcanization accelerators, i.e., additional sulfur donors, may be used herein, e.g., benzothiazoles, alkyl thiuram disulfides, guanidine derivatives and thiocarbamates. Specific representatives of these accelerators include mercapto benzothiazole, tetramethyl thiuram disulfide, benzothiazole disulfide, diphenylguanidine, zinc dithiocarbamate, alkylphenoldisulfide, zinc butyl xanthate, N-dicyclohexyl-2-benzothiazolesulfenamide, N-cyclohexyl-2-benzothiazolesulfenamide, N-oxydiethylenebenzothiazole-2-sulfenamide, N,N-diphenylthiourea, dithiocarbamylsulfenamide, N,N-diisopropylbenzothiazole-2-sulfenamide, zinc-2-mercaptotoluimidazole, dithiobis(N-methyl piperazine), dithiobis(N-beta-hydroxy ethyl piperazine) and dithiobis(dibenzyl amine). Other sulfur donors include, e.g., thiuram and morpholine derivatives. Specific representatives of such donors include dimorpholine disulfide, dimorpholine tetrasulfide, tetramethyl thiuram tetrasulfide, benzothiazyl-2,N-dithiomorpholide, thioplasts, dipentamethylenethiuram hexasulfide and disulfidecaprolactam.

[0074] Accelerators are used to control the time and/or temperature required for vulcanization and to improve the properties of the vulcanizate. In one embodiment, a single accelerator system may be used, i.e., a primary accelerator. Conventionally, a primary accelerator is used in total amounts ranging from 0.5 to 4, and preferably from 0.8 to 1.5, phr. Combinations of primary and a secondary accelerators can also be used with the secondary accelerator being present in smaller amounts, e.g., from 0.05 to about 3 phr, in order to activate and to improve the properties of the vulcanizate. Delayed action accelerators and/or vulcanization retarders may also be used. Suitable types of accelerators are amines, disulfides, guanidines, thioureas, thiazoles, thiurams, sulfenamides, dithiocarbamates and xanthates. In one embodiment, the primary

accelerator is a sulfenamide. If a second accelerator is used, the secondary accelerator can be a guanidine, dithiocarbamate or thiuram compound.

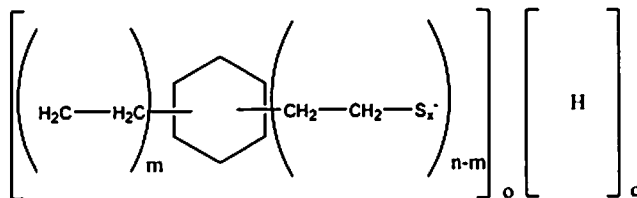
[0075] Typical amounts of tackifier resins, if used, are from 0.5 to 10 phr, and preferably from 1 to 5 phr. Typical amounts of processing aids are 1 to 50 phr. Suitable processing aids include, e.g., aromatic, naphthenic and/or paraffinic processing oils. Typical amounts of antioxidants are from 1 to 5 phr. Representative antioxidants include diphenyl-p-phenylenediamine and others, such as, for example, those identified in the "Vanderbilt Rubber Handbook" (1978), pages 344-346. Typical amounts of antiozonants are from 1 to 5 phr. Typical amounts of fatty acids, e.g., stearic acid, if used are from 0.5 to 3 phr. Typical amounts of zinc oxide are from 2 to 5 phr. Typical amounts of waxes, e.g., microcrystalline waxes, are from 1 to 5 phr. Typical amounts of peptizers, e.g., pentachlorothiophenol and dibenzamidodiphenyl disulfide, are from 0.1 to 1 phr.

[0076] The cured rubber compositions of this invention can be used for various purposes such as the manufacture of tires, weather stripping, hose, belts, seals, gaskets, shoe soles, and the like. In one embodiment of the present invention, the rubber compositions described herein are particularly useful for manufacturing tire treads but can be used for all other parts of a tire as well. The tires can be built, shaped, molded and cured by any of various methods which are well known to those skilled in the art.

[0077] The examples presented illustrate the synthesis of crosslinked polysulfide-containing cycloaliphatic compounds herein and their use as crosslinkers for filled sulfur-vulcanizable elastomer compositions.

#### EXAMPLE 1

[0078] This example illustrates the preparation of a crosslinked polysulfide-containing compound wherein the repeat unit is based upon 1,2,4-trivinylcyclohexane whose structure is:



[0079] Thioacetic acid (1,974 grams, 25.9 mol.) was charged into a 5-liter round bottom flask. Air was bubbled into the thioacetic acid using a fritted tube. 1,2,4-Trivinylcyclohexane (1,303 grams, 8.0 mol.) was added dropwise using an addition funnel over a period of 2.5 hours. An exotherm was observed. The temperature was maintained at 32°C using an ice bath. After 4 hours, the ice bath was removed and the reaction mixture was stirred for an additional 16 hours while air was bubbled through the reaction mixture. The excess thioacetic acid was removed by stripping the solution under vacuum at approximately 100°C. The yield was quantitative, producing 3,137 grams of product. GC analysis confirmed that the reaction was complete.

[0080] The acyl group was removed by the transesterification reaction. The S,S,S-[2,2,2-(1,2,4-cyclohexanetriyl)triethyl]tristhioacetate intermediate (3,090 grams, 7.9 mol.) was charged to a 5-liter round bottom flask. Ethanol (1,070 grams, 23.3 mol.) and sodium ethoxide (68.6 grams) were added with stirring. The mixture was heated to refluxing conditions for 4 hours and the ethyl acetate that formed was removed by distillation at atmospheric pressure. An additional amount of ethanol (672 grams, 15.6 mol.) was added and the mixture was refluxed overnight. The ethanol and ethyl acetate were removed by distillation. The addition of ethanol and removal of ethanol and ethyl acetate were repeated two more times. The 1,2,4-tris(2-mercaptoethyl)cyclohexane intermediate (1,884 grams) was a pale yellow hazy liquid.

[0081] 1,2,4-Tris(2-mercaptoethyl)cyclohexane (238 grams, 0.9 mol.) and cyclohexane (1,582 grams) were charged into a 5 liter round bottom flask. The solution was purged with nitrogen gas and cooled to approximately 15°C with cold water. Sulfur monochloride (S<sub>2</sub>Cl<sub>2</sub>, 182 grams, 1.35 mol.) was added slowly with stirring over 1.75-hour period and then allowed to stand at room temperature for an additional half hour.

A yellow powdery solid formed. The solid was filtered and washed with additional cyclohexane. Nitrogen gas was passed through the filter bed of solids overnight to dry them. The weight of the fluffy, yellow solids was 325 grams.

#### COMPARATIVE EXAMPLE 1 AND EXAMPLES 2 AND 3

[0082] The compounds in Table 1 were mixed in an instrumented "OOC" BANBURY<sup>®</sup> mixer with a 2,600 cubic centimeter chamber volume. The mixing of the rubber was done in three steps. The mixer was turned on with the mixer at 80 rpm and the cooling water at 71°C. The rubber polymers were added to the mixer and ram down mixed for 30 seconds. The fillers and the silane were added to the mixer and ram down mixed for 30 seconds. The other ingredients of the rubber compound of Table 1 except for the oils were added to the mixer and ram down mixed for 60 seconds. The mixer speed was reduced to 65 rpm and then the oils were added to the mixer and ram down mixed for 60 seconds. The mixer throat was dusted down and the ingredients ram down mixed until the temperature reached 150°C. The ingredients were then mixed for an additional 3 minutes and 30 seconds. The mixer speed was adjusted to hold the temperature between 150°C and 155°C. The rubber was dumped (removed from the mixer), a sheet was formed on a roll mill set at about 85°C to 90°C, and then allowed to cool to ambient temperature.

[0083] In the second step, the rubber compound of the first step was recharged into the mixer. The mixer's speed was 80 rpm, the cooling water was set at 71°C and the ram pressure was set at 25 psi. The mixture was ram down mixed for 150 seconds while the temperature was brought up to 150°C, and then the mixer was reduced to 50 rpm. The rubber was mixed for 40 seconds at temperatures between 150°C and 155°C. After mixing, the rubber was dumped (removed from the mixer) and a sheet was formed on a roll mill set at about 85°C to 90°C. The rubber was allowed to cool to ambient temperature.

[0084] In a third step, the mixer speed was set to 50 rpm, the cooling water was set at 71°C and the ram pressure was set at 25 psi. The rubber compound of the second step

and the curatives were ram down mixed for 190 seconds while the temperature of the final mixture was brought up to 115°C. After mixing, the rubber was dumped (removed from the mixer), a sheet was formed on a roll mill set at about 85°C to 90°C, and then allowed to cool to ambient temperature. The curing condition was 160°C for 20 minutes.

[0085] The performance of the sulfur-containing cycloaliphatic compounds of the present invention is demonstrated in a truck tread composition. The formulations of the truck tread tire compositions are set forth in Table 1 and the test results are presented in Table 2. The test procedures were described in the following ASTM and DIN methods:

Mooney Scorch	ASTM D1646
Mooney Viscosity	ASTM D1646
Rheometer (MDR 2000)	DIN 53 529
Storage Modulus, Loss Modulus,	
Tensile and Elongation	DIN 53 504-R1
Shore A Hardness	DIN 53 505
Rebound	DIN 53 512, ASTM D1054
DIN Abrasion	DIN 53 516

Table 1. Truck Tread Rubber Compositions

Ingredients	Comp. Ex. 1	Ex. 2	Comp. Ex. 2	Ex. 3
	phr	phr	phr	phr
Natural rubber	100	100	100	100
Carbon Black	46	46	46	46
Process aid	2.4	2.4	2.4	2.4
Anti-aging	1	1	1	1
Stearic Acid	2	2	2	2
Zinc Oxide	3	3	3	3
Sulfur	1.2	1.2	2.6	2.6
TBBS	1.2	0.87	0.55	0.45
Crosslinker from Ex. 1		4.08		1.36

[0086] The commercial sources of the components of the tread formulations of Table 1 are as follows: natural rubber: (SMR-L); carbon black (N-220); ZnO: Kadox 720C from ZincCorp.; stearic acid: Industrene R from Witco, Crompton; TBBS: Delac NS from Uniroyal, Crompton; sulfur: Rubbermakers Sulfur 104 from Harwick.

Table 2. Truck Tread Rubber Composition Test Results

Rubber Composition, Property	Units	Comp. Ex. 1	Ex. 2	Comp. Ex. 2	Ex. 3
Specific Gravity	g/cm <sup>3</sup>	1.097	1.099	1.095	1.096
MDR 2000 at 160°C					
Time (Cure state) - 10	Min.	2.99	2.05	3.27	2.8
Time (Cure state) - 95	Min.	6.16	6.72	8.03	8.38
ML	dNm	2.66	2.74	2.46	2.57
MHF	dNm	16.02	14.74	15.26	14.96
MHF-ML	dNm	13.36	12.00	12.80	12.39
50% Modulus	MPa	1.145	1.135	1.058	1.055
300% Modulus	MPa	12.686	11.833	12.788	12.417
Tensile	MPa	24.515	22.104	23.648	23.580
Elongation	%	522	508	498	511
Shore A RT	Shore A	60.2	60.1	59.55	59.05
Resilience RT	%	44.6	42.6	45.7	44.1
Rebound 70°C	%	60.2	55.1	57.3	58.0
HSTE	MJ/m <sup>3</sup>	7.58	10.33	7.14	8.5
LTA RT Monsanto (life time analysis)					
Applied strain	Percent	30	30	30	30
Cycle (median)	KC	68	78.9	95.5	106
Variation coefficient	%	14.3	9.9	4.6	8.7
Graves 100°C tear resistance	N/mm	65.93	81.38	62.23	85.18

[0087] The cured truck tread rubber composition had a significant improvement in Graves tear resistance. For example, Example 3 has a 37 percent improvement in Graves tear resistance, when compared to the control formulation without the crosslinker from Example 1 (Comparative Example 2).

[0088] Although the rubber compositions referred to in the examples above have been described as truck tread compositions, these rubber compositions are expected to be suitable for other industrial rubber-based goods, including, illustratively, for conveyor belts.

#### EXAMPLE 4

[0089] A model shoe sole formulation as described in Table 3 below and a mix procedure are used to evaluate representative examples of the thiocarbamoyldisulfanyl-functional cycloaliphatic compounds of the present invention. The mixing is done as follows in a "B" BANBURY® (Farrell Corp.) mixer with a 103-cubic inch (1,690-cubic centimeter) chamber volume. The mixing of the rubber is done in two steps. The first step is to prepare a rubber compound without curatives. The mixer is turned on with the mixer at speed number 2 and full cooling water. The rubber polymers are added to the mixer and ram down mixed for 30 seconds. Half of the silica is added to the mixer and is ram down mixed for 30 seconds. Half of the silica and the oil are added to the mixer and is ram down mixed for 30 seconds. All of the remaining ingredients of the rubber compound are added to the mixer and are ram down mixed for 30 seconds. The mixer is dust down and is ram down mixed for 15 seconds, and then the speed is increased to number 3 and is ram down mixed for an additional 15 seconds. The rubber is dumped (removed from the mixer), a sheet is formed on a roll mill set at about 49°C to 55°C, and then is allowed to cool to ambient temperature.

[0090] In the second step, the final mixture is prepared. The compound of the first step is recharged into the roll mill at about 49°C to 55°C and the curative package is added. The curative package is mixed in and then cut six times on each side. A sheet is formed on a roll mill set and then is allowed to cool to ambient temperature.

Table 3. Model Shoe Sole Formulation

Example 4	
Ingredients	Phr
Natural rubber	20
Nitrile rubber	20
Cis-Butyl rubber	60
Silica	42
Diethylene glycol	2
BHT	1
Zinc Oxide	4.0
Stearic acid	1
Activator	1.5
Disperser	2.0
Homogenizer	2
Wax	1.0
Silane	1.5
Sulfur	2
MBTS	1.0
MBT	0.2
TMTM	0.15
Crosslinker from Example 1	2.5

[0091] The commercial sources of the components of the shoe sole formulations of Table 3 are as follows: cis-butadiene rubber: Budene 1207 from Goodyear Corporation; natural rubber: (SMR-L); nitrile rubber: Perbunan NT 2445 form Bayer; silica: HiSil 233 form PPG; diethylene glycol from Dow Corporation; BHT: butylated hydroxytoluene from Asia Pacific; ZnO: Kadox 720C from ZincCorp.; stearic acid: Industrene R from Witco, Crompton; wax: Sunolite 240 from Witco Corporation; activator: Rhenofit 2555 from Rhein-Chemie; dispenser: Aflux 12 from Rhein-Chemie; homogenizer: Phenosin N260 from Rhein-Chemie; sulfur: Rhenogran S-80 from Rhein-Chemie; MBTS: Thiofide from Flexsys; MBT: Thiotax MBT from Flexsys; TMTM: Rhenogran TMTM

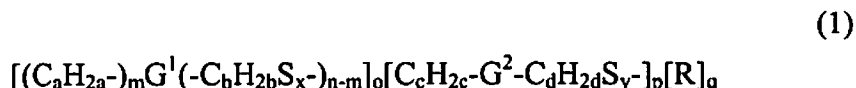


form Rhein-Chemie; silane: Silquest A-1289 silane from Momentive Performance Materials.

[0092] Other embodiments of the invention will be apparent to those skilled in the art from a consideration of this specification or practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with the true scope and spirit of the invention being defined by the following claims.

**CLAIMS:**

1. A crosslinked polysulfide-containing cycloaliphatic compound of the general formula:



wherein  $G^1$  is a saturated, monocyclic aliphatic group of valence  $n$  containing from 5 to 12 carbon atoms and optionally containing at least one halogen or a saturated monocyclic silicone  $[RSiO-]_n[R_2SiO-]_r$  group of valence  $n$ ;  $G^2$  is a saturated, divalent cyclic aliphatic group of valence 2 containing from 5 to 12 carbon atoms and optionally containing at least one halogen or a saturated monocyclic silicone  $[RSiO-]_n[R_2SiO-]_r$  group of valence  $n$ ; each  $R$  independently is a selected from the group consisting of a hydrogen atom, monovalent hydrocarbon of up to 20 carbon atoms and a halogen atom; each occurrence of subscripts  $a, b, c, d, m, n, o, p, q, x$  and  $y$  independently is an integer wherein  $a$  is 2 to 6;  $b$  is 2 to 6;  $c$  is 1 to 6;  $d$  is 1 to 6;  $m$  is 1 or 2;  $n$  is 3 to 5;  $o$  is a positive integer,  $p$  is 0 or a positive integer;  $q$  is a positive integer;  $r$  is an integer of from 0 to 3;  $x$  is 1 to 10 and  $y$  is 1 to 10, with the provisos that,

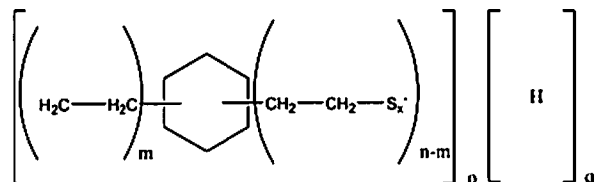
- (i) at least one  $x$  is 2 to 10;
- (ii) the ratio of  $p$  to  $o$  is less than 1 to 5; and
- (iii)  $q$  is equal to the sum of unfilled valences of the  $(C_aH_{2a})_mG^1(-C_bH_{2b}S_x)_{n-m}$  and  $C_cH_{2c}-G^2-C_dH_{2d}S_y$  groups.

2. The crosslinked polysulfide-containing cycloaliphatic compound of Claim 1 wherein each  $G^1$  and  $G^2$  independently is cyclopentane, cyclohexane or cycloheptane group, optionally containing at least one chlorine.

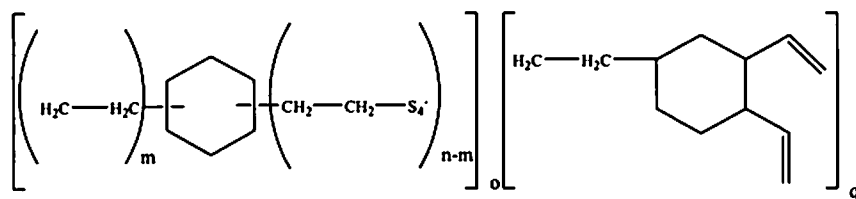
3. A mixture of stereoisomers of the polysulfide-containing cycloaliphatic compound of Claim 1 wherein at least 50 weight percent of the mixture is isomer in which the polysulfide groups are in the equatorial position relative to group  $G^1$  and  $G^2$ .

4. The crosslinked polysulfide-containing cycloaliphatic compound of Claim 1 wherein each R independently is selected from the group consisting of hydrogen, and chlorine, divinylcyclohexylethyl.

5. The crosslinked polysulfide-containing cycloaliphatic compound of Claim 1 which is at least one member of the group consisting of:



where each m is independently 1 or 2, n is 3, each o and q independently is a positive integer, each x independently an integer from 2 to 6 and the substitution on the ring is 1,2 and 4;



where each m is independently 1 or 2, n is 3, each o and q independently is a positive integer and the substitution on the ring is 1, 2, 4; and,

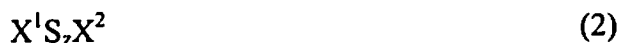


where D represents a RSiO- unit, each m is independently 1 or 2, n is 3, each o and q independently is a positive integer and the substitution on the ring occurs on the silicon atoms

6. A process for preparing the crosslinked polysulfide-containing cycloaliphatic compound of Claim 1, and mixtures thereof, which comprises:

- a) reacting poly-alkenyl-substituted cycloalkane with thioacid in the presence of a free-radical source to provide poly-thiocarboxylate-substituted alkylcycloalkane;

- b) reacting poly-thiocarboxylate-substituted alkylcycloalkane with deblocking agent to form free poly-mercaptan-functional alkylcycloalkane;
- c) reacting the free poly-mercaptan-functional alkylcycloalkane with an oxidizing agent selected from halogenated sulfur-containing compound represented by the general formula:



wherein  $X^1$  is chlorine, bromine or iodine atom,  $X^2$  is  $X^1$ , hydrogen or a hydrocarbon of up to 12 carbon atoms, and z independently an integer wherein z is 1 to 10; peroxides; hydroperoxides; and oxygen,

to provide crosslinked polysulfide-containing cycloaliphatic compound.

7. A filled sulfur-vulcanizable elastomer composition which comprises:
  - (i) at least one sulfur-vulcanizable elastomer;
  - (ii) at least one particulate filler; and,
  - (iii) a crosslinking effective amount of, as crosslinker for sulfur-vulcanizable elastomer (i), at least one crosslinked polysulfide-containing cycloaliphatic compound of Claim 1.

8. The filled sulfur-vulcanizable elastomer composition of Claim 7 wherein sulfur-vulcanizable elastomer (i) is at least one member selected from the group consisting of cis-1,4-polyisoprene rubber, emulsion polymerization-prepared styrene/butadiene copolymer rubber, organic solution polymerization-prepared styrene/butadiene rubber, 3,4-polyisoprene rubber, isoprene/butadiene rubber, styrene/isoprene/butadiene terpolymer rubber, cis-1,4-polybutadiene rubber, medium vinyl polybutadiene rubber, high vinyl polybutadiene rubber, styrene/isoprene copolymer, emulsion polymerization-prepared styrene/butadiene/acrylonitrile terpolymer rubber, butadiene/acrylonitrile copolymer rubber, emulsion polymerization-derived

styrene/butadiene (ESBR) having a styrene content of from 20 to 28 percent bound styrene, and an ESBR having a bound styrene content of from 30 to 45 percent.

9. The filled sulfur-vulcanizable elastomer composition of Claim 7 wherein particulate filler (ii) is at least one member selected from the group consisting a filler that is reactive for silane, the filler being combined with at least one silane possessing functionality that is reactive for sulfur-vulcanizable elastomer (i).

10. The sulfur-vulcanizable filled elastomer composition of Claim 9 in which the inert porous filler is carbon and the filler that is reactive for silane is silica.

11. The filled sulfur-vulcanizable elastomer of Claim 9 in which the silane is a silylated core polysulfide.

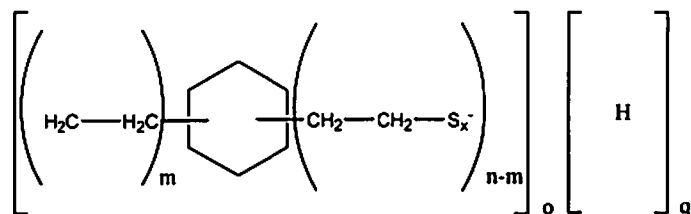
12. The filled sulfur-vulcanizable elastomer of Claim 10 in which the silane is a silylated core polysulfide.

13. The filled sulfur-vulcanizable elastomer composition of Claim 7 wherein in crosslinked polysulfide-containing cycloaliphatic compound (iii), each  $G^1$  and  $G^2$  independently is a cyclopentane, cyclohexane or cycloheptane group, optionally containing at least one chlorine.

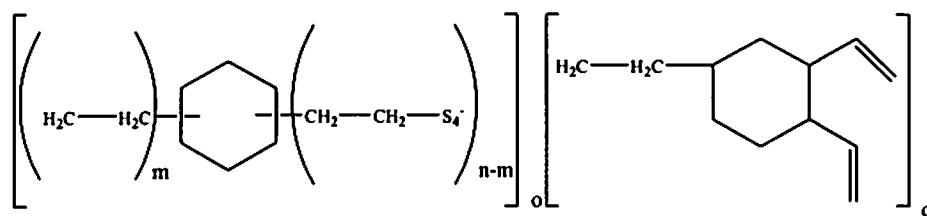
14. The filled sulfur-vulcanizable elastomer composition of Claim 7 wherein crosslinked polysulfide-containing cycloaliphatic compound (iii) is a mixture of stereoisomers wherein at least 50 weight percent of the mixture is isomer in which the polysulfide groups are in the equatorial position relative to group  $G^1$  and/or  $G^2$ .

15. The filled sulfur-vulcanizable elastomer composition of Claim 7 wherein in crosslinked polysulfide-containing cycloaliphatic compound (iii), each R independently is selected from the group consisting of hydrogen, and chlorine, divinylcyclohexylethyl.

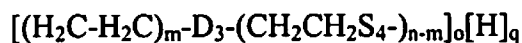
16. The filled sulfur-vulcanizable elastomer composition of Claim 7 wherein sulfur-containing cycloaliphatic compound (iii) is at least one member of the group consisting of:



where each  $m$  is independently 1 or 2,  $n$  is 3, each  $o$  and  $q$  independently is a positive integer, each  $x$  independently an integer from 2 to 6 and the substitution on the ring is 1,2 and 4;



where each  $m$  is independently 1 or 2,  $n$  is 3, each  $o$  and  $q$  independently is a positive integer and the substitution on the ring is 1, 2, 4; and



where  $D$  represents a  $\text{RSiO-}$  unit, each  $m$  is independently 1 or 2,  $n$  is 3, each  $o$  and  $q$  independently is a positive integer and the substitution on the ring occurs on the silicon atoms.

17. The cured composition of Claim 7.

18. The cured composition of Claim 17 provided as a weather stripping, hose, belt, seal, gasket or shoe sole.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2009/062668

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G75/00

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 444 364 A (HILTI AG [LI]) 4 June 2008 (2008-06-04) claims 1-18; examples 1,2 -----	1-18
X	WO 2005/007758 A (MCDANIEL C STEVEN [US]) 27 January 2005 (2005-01-27) claims 1-207; examples 1-20 -----	1-18
X	WO 2004/112482 A (MCDANIEL STEVEN C [US]) 29 December 2004 (2004-12-29) claims 1-321; examples 1-18 -----	1-18
X	US 6 197 888 B1 (LUO STEVEN [US]) 6 March 2001 (2001-03-06) claims 1-20; examples 1-4 -----	1-18
X	EP 0 432 406 A (HUELS CHEMISCHE WERKE AG [DE]) 19 June 1991 (1991-06-19) claims 1-5; example 1 -----	1-18

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

☒ See patent family annex.

\* Special categories of cited documents:

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

11 January 2010

Date of mailing of the international search report

19/01/2010

Name and mailing address of the ISA/

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Authorized officer

Glomm, Bernhard

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2009/062668

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