

Diene elastomer modified by a group comprising a silicon atom, process for the synthesis thereof and rubber composition containing same

5 [0001] The present invention relates to a diene elastomer modified by a group comprising a silicon atom, and bearing another functional group. The present invention also relates to the process for the synthesis thereof and also to a rubber composition, which can be used in particular in the manufacture of tyres, comprising this elastomer and also a reinforcing filler.

10 [0002] Now that savings in fuel and the need to protect the environment have become a priority, it is desirable to produce polymers having good mechanical properties and a hysteresis which is as low as possible in order to be able to process them in the form of rubber compositions which can be used in the manufacture of various semi-finished products participating in the forming of tyres. Many solutions have already been experimented with
15 in order to achieve the objective of a fall in hysteresis. Mention may in particular be made of the modification of the structure of diene polymers and copolymers for the purpose of polymerization by means of functionalization agents, with the aim of obtaining a good interaction between the polymer, thus modified, and the filler, whether carbon black or
20 another reinforcing filler. Provision has in particular been made to use diene polymers functionalized by alkoxysilane derivatives.

[0003] Mention may be made, by way of illustration of this prior art relating to such modifications, for example, of United States Patent US-A-5 066 721, which describes a rubber composition comprising a diene polymer
25 functionalized by an alkoxysilane having at least one non-hydrolysable alkoxyl residue as a mixture with silica. Mention may also be made of Patent Application EP A 0 299 074, which describes functionalized polymers comprising alkoxysilane functional groups at the chain end. These functionalized polymers have been described in the prior art as effective in
30 reducing hysteresis and improving abrasion resistance; however, their

properties remain insufficient to allow the processing of these polymers in compositions intended to constitute treads of tyres.

[0004] Provision has also been made to combine the functionalization by alkoxy silane functional groups with the functionalization by other functional groups, in particular the amine functional group. Thus, Patent EP 0 992 537 describes a rubber composition which comprises an extended elastomer modified at the chain end by an alkoxy silane functional group and bearing, at the other end or along its chain, one or more amine functional groups. Furthermore, provision has also been made to improve the properties of rubber compositions by using elastomers functionalized at the chain end by alkoxy silane functional groups bearing an amine group, whether this is as black, silica or hybrid mixture. Mention may be made, for example, of Patent Application US 2005/0203251, which describes a rubber composition reinforced by silica comprising an elastomer functionalized at the chain end by an alkoxy silane bearing an amine group.

[0005] From the perspective of improving the mechanical and dynamic properties of rubber compositions intended for a tyre application, in particular the hysteresis, while retaining a satisfactory raw processing, the Applicant Company has provided, in the document WO 2009133068 A1, for a functionalized diene elastomer essentially formed of the coupled entity of a modified elastomer having, within the chain, an alkoxy silane group bearing an amine functional group, the silicon atom of this alkoxy silane group linking the two parts of the main chain of the diene elastomer.

[0006] Furthermore, it turns out that, under certain storage conditions before use in a rubber composition, the ageing of the elastomers modified with alkoxy silane groups bearing another functional group, in particular an amine group, results in their microstructure being highly modified.

[0007] The inventors believe, without being committed to this interpretation alone, that these modified elastomers exhibit an instability on storage as a result of the hydrolysis and condensation reactions of the alkoxy silane

groups, which thus bring about a change in the macrostructure of the elastomer.

[0008] The technical problem which the present invention intends to solve is that of stabilizing the macrostructure of the modified elastomers comprising alkoxy silane groups bearing in particular another functional group, by slowing down the change therein, indeed even by halting it, without damaging the manufacture thereof or the properties which these elastomers confer on the rubber compositions containing them. It is also advisable to solve this problem while remaining within the context of a process which is economically advantageous from an industrial viewpoint.

[0009] This aim is achieved in that the Inventors have now demonstrated that a diene elastomer modified with a specific functionalization agent is stable on storage in so far as it does not exhibit a significant change in macrostructure during storage for at least one month. The synthesis of such a modified elastomer remains economically advantageous in the context of an industrial use.

[0010] A subject-matter of the invention is thus a modified diene elastomer comprising, within its structure, at least one alkoxy silane group, the silicon atom of which forms part of the main chain of the elastomer and the silicon atom of which is, in addition, substituted by at least one other functional group comprising a nitrogen atom bonded to the silicon atom via a spacer group defined as being a saturated linear divalent aliphatic hydrocarbon radical having at least 5 carbon atoms, preferably at least 6, and at most 10 carbon atoms, preferably at most 9, preferentially a saturated linear divalent C₆, C₇, C₈ or C₉ aliphatic hydrocarbon radical. According to some alternative forms, the spacer group is preferably a saturated linear divalent C₆ aliphatic hydrocarbon radical and, according to other alternative forms, the spacer group is a saturated linear divalent C₇, C₈ or C₉ aliphatic hydrocarbon radical.

[0011] Another subject-matter of the invention is a process for the synthesis of such a modified diene elastomer comprising the reaction of a living diene elastomer, resulting from the polymerization of at least one diene monomer, with a specific functionalization agent chosen from alkoxysilane compounds comprising another functional group comprising a nitrogen atom bonded to the silicon atom via a spacer group defined as being a saturated linear divalent aliphatic hydrocarbon radical having at least 5 carbon atoms, preferably at least 6, and at most 10 carbon atoms, preferably at most 9, preferentially a saturated linear divalent C₆, C₇, C₈ or C₉ aliphatic hydrocarbon radical. According to some alternative forms, the spacer group is preferably a saturated linear divalent C₆ aliphatic hydrocarbon radical and, according to other alternative forms, the spacer group is a saturated linear divalent C₇, C₈ or C₉ aliphatic hydrocarbon radical.

[0012] A further subject-matter of the invention is a modified diene elastomer directly obtained by this synthesis process.

[0013] Another subject-matter of the invention is a rubber composition based on at least one modified diene elastomer in accordance with the invention.

[0014] Another subject-matter of the invention is a tyre which comprises a rubber composition in accordance with the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0015] In the present description, unless expressly indicated otherwise, all the percentages (%) shown are % by weight. The abbreviation "phr" means parts by weight per hundred parts of elastomers present in the elastomer matrix, the elastomer matrix denoting all of the elastomers present in the rubber composition.

[0016] Furthermore, any interval of values denoted by the expression "between a and b" represents the range of values greater than "a" and lower than "b" (that is to say, limits a and b excluded), whereas any interval

of values denoted by the expression "from a to b" means the range of values extending from "a" up to "b" (that is to say, including the strict limits a and b). In the present document, when an interval of values is denoted by the expression "from a to b", the interval represented by the expression "between a and b" is also and preferably denoted.

[0017] In the present patent application, "predominantly" or "predominant", in connection with a compound, is understood to mean that this compound is predominant among the compounds of the same type in the composition, that is to say that it is the one which represents the biggest fraction by weight among the compounds of the same type. Thus, for example, a predominant elastomer is the elastomer representing the greatest fraction by weight, with respect to the total weight of the elastomers in the composition. In the same way, a "predominant" filler is that representing the greatest fraction by weight, with respect to the total weight of the combined fillers of the composition. Also, a "predominant" population of elastomer functional chain is that representing the greatest fraction by weight among the chains constituting the diene elastomer, with respect to the total weight of the diene elastomer. In a system comprising just one compound of a certain type, the latter is predominant within the meaning of the present invention.

[0018] The expression "composition based on" should be understood as meaning, in the present description, a composition comprising the mixture and/or the in situ reaction product of the various constituents used, some of these base constituents (for example the elastomer, the filler or other additive conventionally used in a rubber composition intended for the manufacture of tyres) being capable of reacting or intended to react with one another, at least in part, during the various phases of manufacture of the composition intended for the manufacture of tyres.

[0019] In the present description, modified diene elastomer is understood to mean a diene elastomer which comprises a group comprising one or more heteroatoms, including a silicon atom, the latter being located in the main

chain of the elastomer including the terminal positions of the main chain (or chain ends).

5 [0020] This group can be located at the end of the linear main elastomer chain. It will then be said that the diene elastomer is functionalized at the chain end. It is generally an elastomer obtained by reaction of a living elastomer with a functionalization agent, that is to say any molecule comprising at least one chemical group known by a person skilled in the art to react with a living chain end.

10 [0021] This group can be located in the linear main elastomer chain. It will then be said that the diene elastomer is coupled or else functionalized in the middle of the chain, in contrast to the position "at the chain end" and although the group is not located precisely at the middle of the elastomer chain. It is generally an elastomer obtained by reaction of a living elastomer with a coupling agent, that is to say any molecule comprising at least two
15 chemical groups known by a person skilled in the art to react with a living chain end.

[0022] A person skilled in the art will understand that, generally, a functionalization reaction with an agent of alkoxysilane type comprising more than one alkoxy functional group which is reactive with respect to the
20 living elastomer results in an elastomer mixture, the composition of which depends on the operating conditions, mainly the molar ratio of the functionalization agent to the living chains, and on the number of these reactive functional groups. The mixture can comprise elastomers functionalized at the chain end, elastomers functionalized in the middle of
25 the chain and, if appropriate, star-branch elastomers and also non-functionalized elastomers. The elastomers functionalized at the chain end and in the middle of the chain are capable of comprising an alkoxysilane group.

[0023] In the present description, the expression "monomer unit", whether it is diene or other, is understood as a unit of the polymer resulting from the monomer in question.

5 [0024] It should be noted that, in the context of the invention, the monomers used can be of fossil or biosourced origin. In the latter case, they may partially or completely result from biomass or be obtained from renewable starting materials resulting from biomass.

10 [0025] A subject-matter of the invention is thus a modified diene elastomer, within the main chain, a silicon atom substituted, on the one hand, by at least one alkoxy group, optionally partially or completely hydrolysed to give a hydroxyl group, and, on the other hand, by at least one other functional group comprising a nitrogen atom bonded to the silicon atom via a spacer group chosen from saturated linear acyclic divalent aliphatic hydrocarbon radicals having at least 5 carbon atoms, preferably at least 6, and at most 15 10 carbon atoms, preferably at most 9.

[0026] Diene elastomer should be understood, in a known way, as meaning an elastomer resulting at least in part (i.e., a homopolymer or a copolymer) from diene monomers (monomers bearing two conjugated or non-conjugated carbon-carbon double bonds). More particularly, diene elastomer according to the invention is understood to mean any 20 homopolymer obtained by polymerization of a conjugated diene monomer having from 4 to 12 carbon atoms, or any copolymer obtained by copolymerization of one or more conjugated dienes with one another or with one or more ethylenically unsaturated monomers (comprising a carbon-carbon double bond), including aliphatic mono-olefins, such as ethylene and 25 aliphatic α -olefins having from 3 to 18 carbon atoms, and vinylaromatic compounds having from 8 to 20 carbon atoms. In the case of copolymers obtained by copolymerization with one or more ethylenically unsaturated monomers, these copolymers contain from 20% to 99% by weight of diene units and from 1% to 80% by weight of units resulting from ethylenically 30 unsaturated monomers.

[0027] The following are suitable in particular as conjugated dienes in accordance with the invention: 1,3-butadiene, 2,3-di(C₁ to C₅ alkyl)-1,3-butadienes, such as, for example, 2,3-dimethyl-1,3-butadiene, 2,3-diethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-butadiene or 2-methyl-3-isopropyl-1,3-butadiene, phenyl-1,3-butadiene, isoprene, 1,3-pentadiene and 2,4-hexadiene, and the like. Advantageously, the conjugated diene is 1,3-butadiene or isoprene, preferably 1,3-butadiene.

[0028] For example, an aliphatic α -olefin having from 3 to 18 carbon atoms, advantageously having from 3 to 6 carbon atoms, is suitable as aliphatic α -olefin monomer. Mention may be made of propylene, butene, pentene, hexene or a mixture of these compounds.

[0029] The following in particular are suitable as vinylaromatic monomers: styrene, ortho-, meta- or para-methylstyrene, α -methylstyrene, the "vinyltoluene" commercial mixture, para-(tert-butyl)styrene, methoxystyrenes, vinylmesitylene, divinylbenzene and vinylnaphthalene, and the like. Advantageously, the vinylaromatic monomer is styrene.

[0030] The diene elastomer is preferably selected from the group of the diene elastomers consisting of polybutadienes (BRs), synthetic polyisoprenes (IRs), butadiene copolymers, in particular copolymers of butadiene and of a vinylaromatic monomer or copolymers of butadiene and of an aliphatic mono-olefin, isoprene copolymers and the mixtures of these elastomers. Such copolymers are more particularly butadiene/styrene copolymers (SBRs), butadiene/ethylene copolymers (EBRs), isoprene/butadiene copolymers (BIRs), isoprene/styrene copolymers (SIRs) and isoprene/butadiene/styrene copolymers (SBIRs). Among these copolymers, butadiene/styrene copolymers (SBRs) are particularly preferred.

[0031] The diene elastomer can have any microstructure which depends on the polymerization conditions used. The elastomer can be block, random, sequential, microsequential, and the like.

[0032] The modified diene elastomer according to the invention comprises, within its structure, at least one alkoxysilane group, optionally partially or completely hydrolysed to give silanol, the silicon atom of which forms part of the main chain of the elastomer and is in addition substituted by another functional group comprising a nitrogen atom bonded to the silicon atom via a spacer group.

[0033] When the alkoxysilane group is located at the main chain end, it can be a monoalkoxysilane or a dialkoxysilane, that is to say that the silicon atom can be substituted by one or two alkoxy groups, optionally partially or completely hydrolysed to give a hydroxyl group.

[0034] When the alkoxysilane group is located in the middle of the main chain, it is a monoalkoxysilane, that is to say that the silicon atom is substituted by an alkoxy group, optionally partially or completely hydrolysed to give a hydroxyl group.

[0035] The alkoxy groups of the alkoxysilane group can, according to some alternative forms of the invention, be partially or completely hydrolysed to give hydroxyl groups. According to these alternative forms, all or at least 50 mol% of the alkoxy functional groups borne by the modified diene elastomer are hydrolysed to give hydroxyl groups. In particular, at least 80 mol% of the alkoxy functional groups borne by the modified diene elastomer are hydrolysed to give hydroxyl groups, indeed even 100%.

[0036] The alkyl radicals of the alkoxy groups substituting the silicon atom are, independently of one another, chosen from C_1 - C_{10} , indeed even C_1 - C_8 , alkyl radicals, preferably from C_1 - C_4 alkyl radicals, more preferably from methyl and ethyl.

[0037] According to the invention, the silicon atom of the alkoxysilane group is in addition substituted by at least one other functional group comprising a nitrogen atom bonded to the silicon atom via a spacer group chosen from saturated linear divalent aliphatic hydrocarbon radicals having at least 5 carbon atoms, preferably at least 6, and at most 10 carbon atoms,

preferably at most 9. This spacer group is, according to alternative forms of the invention, chosen from saturated linear divalent C₆, C₇, C₈ or C₉ aliphatic hydrocarbon radicals. According to some alternative forms, the spacer group is preferably a saturated linear divalent C₆ aliphatic hydrocarbon radical and, according to other alternative forms, the spacer group is a saturated linear divalent C₇, C₈ or C₉ aliphatic hydrocarbon radical.

[0038] This characteristic relating to the nature of the spacer group is particularly important in the context of the invention and contributes, significantly and unexpectedly, to the stabilization of the macrostructure of the modified diene elastomer during storage. Below 5 carbon atoms in the spacer group, satisfactory stabilization of the macrostructure is not observed.

[0039] According to the invention, the spacer group bonds, to the silicon atom of the alkoxy silane group, at least one other functional group comprising a nitrogen atom. According to alternative forms of the invention, this functional group can be a cyclic or non-cyclic, tertiary, protected or unprotected secondary or protected or unprotected primary amine, an isocyanate, an imine or a cyano. When the functional group is an amine, the latter is preferably a tertiary amine.

[0040] Mention may thus be made, as secondary or tertiary amine functional group, of amines substituted by C₁-C₁₀ alkyl, preferably C₁-C₄ alkyl, radicals, more preferably a methyl or ethyl radical, or else of cyclic amines forming a heterocycle containing a nitrogen atom and at least one carbon atom, preferably from 2 to 6 carbon atoms. For example, the methylamino-, dimethylamino-, ethylamino-, diethylamino-, propylamino-, dipropylamino-, butylamino-, dibutylamino-, pentylamino-, dipentylamino-, hexylamino-, dihexylamino- or hexamethyleneamino- groups, preferably the diethylamino- and dimethylamino- groups, are suitable.

[0041] Mention may be made, as imine functional group, of ketimines. For example, the (1,3-dimethylbutylidene)amino-, (ethylidene)amino-, (1-methylpropylidene)amino-, (4-N,N-dimethylaminobenzylidene)amino-, (cyclohexylidene)amino-, dihydroimidazole and imidazole groups are suitable.

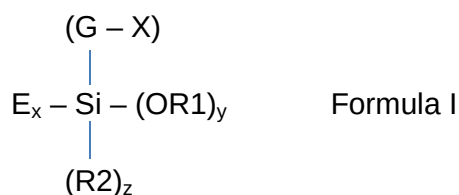
[0042] According to preferred alternative forms of the invention, the other functional group is a dialkylamino- tertiary amine, the alkyl radicals of which, independently of one another, are C₁-C₄ alkyl radicals, preferably methyl or ethyl.

[0043] The different preferred alternative forms and aspects relating to the nature of the modified diene elastomer, of the alkoxysilane functional group, of the spacer group and of the other functional group comprising a nitrogen atom can be combined with one another subject to their compatibility.

[0044] According to advantageous alternative forms of the invention, at least one, at least two, at least three, at least four, of the following characteristics is or are observed and preferably all:

- the other functional group is a tertiary amine, more particularly a diethylamino- or dimethylamino- group,
- the spacer group is a saturated linear divalent C₆, C₇, C₈ or C₉, preferably C₆, aliphatic hydrocarbon radical,
- in the alkoxy group or groups substituting the silicon atom, the alkyl radical has from 1 to 4 carbon atoms and is preferably a methyl radical or an ethyl radical,
- at least 50% of the alkoxy functional groups substituting the silicon atom are hydrolysed to give hydroxyl groups,
- the diene elastomer is a butadiene/styrene copolymer.

[0045] According to alternative forms of the invention, the modified diene elastomer can be represented by the following general formula I:



in which:

- 5 - E represents a diene elastomer chain;
- R1 represents a hydrogen atom or a C₁-C₁₀, indeed even C₁-C₈, alkyl radical, preferably a C₁-C₄ alkyl radical, more preferably methyl and ethyl;
- 10 - R2 represents a substituted or unsubstituted C₁-C₁₀, indeed even C₁-C₈, alkyl radical, preferably a C₁-C₄ alkyl radical, more preferably methyl and ethyl;
- G represents a spacer group chosen from saturated linear divalent aliphatic hydrocarbon radicals having at least 5 carbon atoms, preferably at least 6, and at most 10 carbon atoms, preferably at most 9;
- 15 - X represents a functional group comprising a nitrogen atom;
- x has the value 1 or 2, y has the value 1 or 2 and z has the value 0 or 1, with the proviso that x + y + z = 3.

[0046] When y has the value 1, then either x = z = 1 or x = 2 and z = 0.

20 [0047] When y has the value 2, then x = 1 and z = 0.

[0048] According to alternative forms of the invention, G represents a spacer group chosen from saturated linear divalent C₆, C₇, C₈ or C₉ aliphatic hydrocarbon radicals. According to some of these alternative forms, the spacer group is preferably a saturated linear divalent C₆ aliphatic hydrocarbon radical and, according to other alternative forms, the spacer group is a saturated linear divalent C₇, C₈ or C₉ aliphatic hydrocarbon radical.

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[0049] According to alternative forms of the invention, the functional group X can be a cyclic or non-cyclic, tertiary, protected or unprotected secondary or protected or unprotected primary amine, an isocyanate, an imine or a cyano. According to preferred alternative forms of the invention, X is an amine, more preferably a tertiary amine $-NR_2$, the alkyl radicals R of which, independently of one another, are C_1 - C_4 alkyl radicals, preferably methyl or ethyl.

[0050] E is a diene elastomer chain, the nature of which is as defined above. Preferably, E is a polybutadiene (BR), synthetic polyisoprene (IR), butadiene copolymer or isoprene copolymer chain. More particularly among the copolymer chains, E is a butadiene/styrene copolymer (SBR), butadiene/ethylene copolymer (EBR), isoprene/butadiene copolymer (BIR), isoprene/styrene copolymer (SIR) or isoprene/butadiene/styrene copolymer (SBIR) chain. Among these, E is preferably a butadiene/styrene copolymer (SBR) chain.

[0051] The different preferred alternative forms and aspects relating to the nature of E, R1, R2, G, X and R, and also relating to the values of x, y and z, can be combined together subject to their compatibility.

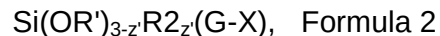
[0052] According to advantageous alternative forms of the invention, at least one, at least two, at least three, at least four of the following characteristics is or are observed and preferably all:

- X is a tertiary amine $-NR_2$ functional group, the alkyl radicals R of which, independently of one another, are C_1 - C_4 alkyl radicals; more particularly, X is a diethylamino- or dimethylamino- group,
- G is a saturated linear divalent C_6 , C_7 , C_8 or C_9 , preferably C_6 , aliphatic hydrocarbon radical,
- the alkyl radical R1 has from 1 to 4 carbon atoms; preferably, R1 is a methyl radical or an ethyl radical,
- at least 50% of the OR1 functional groups are hydrolysed to give OH,
- E is a butadiene/styrene copolymer chain.

[0053] Another subject-matter of the invention is the process for the synthesis of a modified elastomer in accordance with the preceding description.

[0054] Thus, according to the invention, a process for the synthesis of a modified diene elastomer comprising, in the main chain, a silicon atom substituted, on the one hand, by at least one alkoxy group, optionally partially or completely hydrolysed to give a hydroxyl group, and, on the other hand, by at least one other functional group comprising a nitrogen atom bonded to the silicon atom via a spacer group, comprises:

- a) a stage of polymerization of at least one diene monomer,
- b) a stage of modification of the living diene elastomer obtained in the preceding stage by means of at least one functionalization agent corresponding to the following general formula:



in which:

- G is a spacer group chosen from saturated linear divalent aliphatic hydrocarbon radicals having at least 5 carbon atoms, preferably at least 6, and at most 10 carbon atoms, preferably at most 9;
- X represents a functional group comprising a nitrogen atom;
- R', independently of one another, represent a C₁-C₁₀, indeed even C₁-C₈, alkyl group, preferably a C₁-C₄ alkyl group, more preferably methyl and ethyl;
- R₂ represents a C₁-C₁₀, indeed even C₁-C₈, alkyl group, more preferably methyl and ethyl;
- z' has the value 0 or 1.

[0055] According to some alternative forms of the process of the invention, z' has the value 0. According to other alternative forms of the invention, z' has the value 1.

[0056] According to some alternative forms of the invention, G represents a spacer group chosen from saturated linear divalent C₆, C₇, C₈ or C₉ aliphatic hydrocarbon radicals. Preferably, according to these alternative forms, the spacer group is a saturated linear divalent C₆ aliphatic hydrocarbon radical. According to others of these alternative forms, the spacer group is a saturated linear divalent C₇, C₈ or C₉ aliphatic hydrocarbon radical.

[0057] X is a functional group comprising a nitrogen atom. According to alternative forms of the invention, this functional group can be a cyclic or non-cyclic, tertiary, protected or unprotected secondary or protected or unprotected primary amine, an isocyanate, an imine or a cyano.

[0058] According to preferred alternative forms of the process of the invention, the functional group comprising a nitrogen atom is a protected or unprotected primary amine, a protected or unprotected secondary amine or a tertiary amine. The nitrogen atom can then be substituted by two identical or different groups which can be a trialkylsilyl radical, the alkyl group having from 1 to 4 carbon atoms, or a C₁-C₁₀ alkyl, preferably C₁-C₄ alkyl, radical, more preferably a methyl or ethyl radical, or else the two substituents of the nitrogen form, with the latter, a heterocycle comprising a nitrogen atom and at least one carbon atom, preferably from 2 to 6 carbon atoms.

[0059] According to these preferred alternative forms of the invention, X is more preferably still a tertiary amine -NR₂ functional group, the alkyl radicals R of which, independently of one another, are C₁-C₄ alkyl radicals, preferably methyl or ethyl. This is because the use of a functionalization agent comprising a tertiary amine functional group makes it possible to be freed from any additional stage of deprotection of the amines and from its possible side reactions.

[0060] The different preferred alternative forms and aspects relating to the nature of R', R₂, G, X and R, and also relating to the values of z, can be combined together subject to their compatibility.

[0061] According to the alternative forms of the invention where X is an amine functional group, mention may be made, for example, as functionalization agents, of (N,N-dialkylaminohexyl)trialkoxysilanes, (N-alkylaminohexyl)trialkoxysilanes, the secondary amine functional group of which is protected by a trialkylsilyl group, and aminohexyltrialkoxysilanes, the primary amine functional group of which is protected by two trialkylsilyl groups, (N,N-dialkylaminohexyl)dialkoxyalkylsilanes, (N-alkylaminohexyl)dialkoxyalkylsilanes, the secondary amine functional group of which is protected by a trialkylsilyl group, and aminohexyldialkoxyalkylsilanes, the primary amine functional group of which is protected by two trialkylsilyl groups. The alkyl substituents of the nitrogen and silicon atom and also the alkoxy substituents are as described above.

[0062] Preferably, according to these alternative forms of the invention, X is a tertiary amine functional group and the functionalization agent can be chosen from the compounds (6-N,N-dimethylaminohexyl)trimethoxysilane, (6-N,N-dimethylaminohexyl)triethoxysilane, (6-N,N-diethylaminohexyl)trimethoxysilane, (6-N,N-diethylaminohexyl)triethoxysilane, (6-N,N-dimethylaminohexyl)dimethoxymethylsilane, (6-N,N-dimethylaminohexyl)diethoxymethylsilane, (6-N,N-diethylaminohexyl)diethoxymethylsilane and (6-N,N-diethylaminohexyl)dimethoxymethylsilane.

[0063] According to alternative forms of the invention, X is an isocyanate functional group. Preferably, the functionalization agent can be chosen from the compounds (6-isocyanatohexyl)trimethoxysilane, (6-isocyanatohexyl)triethoxysilane, (6-isocyanatohexyl)dimethoxymethylsilane or (6-isocyanatohexyl)diethoxymethylsilane.

[0064] According to alternative forms of the invention, X is an imine functional group. Preferably, the functionalization agent can be chosen from N-(1,3-dimethylbutylidene)-3-(trimethoxysilyl)-1-hexanamine, N-(1,3-

dimethylbutylidene)-3-(triethoxysilyl)-1-hexanamine, N-(1,3-
 dimethylbutylidene)-3-(dimethoxymethylsilyl)-1-hexanamine, N-(1,3-
 dimethylbutylidene)-3-(diethoxymethylsilyl)-1-hexanamine, N-(1,3-
 methyléthylidene)-3-(trimethoxysilyl)-1-hexanamine, N-(1,3-
 5 methylethylidene)-3-(triethoxysilyl)-1-hexanamine, N-(1,3-
 methylethylidene)-3-(dimethoxymethylsilyl)-1-hexanamine, N-(1,3-
 methylethylidene)-3-(diethoxymethylsilyl)-1-hexanamine, N-ethylidene-3-
 (trimethoxysilyl)-1-hexanamine, N-ethylidene-3-(triethoxysilyl)-1-
 hexanamine, N-ethylidene-3-(dimethoxymethylsilyl)-1-hexanamine, N-
 10 ethylidene-3-(diethoxymethylsilyl)-1-hexanamine, N-(1-methylpropylidene)-
 3-(trimethoxysilyl)-1-hexanamine, N-(1-methylpropylidene)-3-(triethoxysilyl)-
 1-hexanamine, N-(1-methylpropylidene)-3-(dimethoxymethylsilyl)-1-
 hexanamine, N-(1-methylpropylidene)-3-(diethoxymethylsilyl)-1-
 hexanamine, N-(4-N,N-dimethylaminobenzylidene)-3-(trimethoxysilyl)-1-
 15 hexanamine, N-(4-N,N-dimethylaminobenzylidene)-3-(triethoxysilyl)-1-
 hexanamine, N-(4-N,N-dimethylaminobenzylidene)-3-
 (dimethoxymethylsilyl)-1-hexanamine, N-(4-N,N-
 dimethylaminobenzylidene)-3-(diethoxymethylsilyl)-1-hexanamine, N-
 (cyclohexylidene)-3-(trimethoxysilyl)-1-hexanamine, N-(cyclohexylidene)-3-
 20 (triethoxysilyl)-1-hexanamine, N-(cyclohexylidene)-3-(dimethoxymethylsilyl)-
 1-hexanamine, N-(cyclohexylidene)-3-(diethoxymethylsilyl)-1-hexanamine,
 N-(3-trimethoxysilylhexyl)-4,5-dihydroimidazole, N-(3-triethoxysilylhexyl)-
 4,5-dihydroimidazole, N-(3-dimethoxymethylsilylhexyl)-4,5-
 dihydroimidazole, N-(3-diethoxymethylsilylhexyl)-4,5-dihydroimidazole, N-
 25 (3-trimethoxysilylhexyl)-4,5-imidazole, N-(3-triethoxysilylhexyl)-4,5-
 imidazole, N-(3-dimethoxymethylsilylhexyl)-4,5-imidazole and N-(3-
 diethoxymethylsilylhexyl)-4,5-imidazole.

[0065] According to alternative forms of the invention, X is a cyano
 functional group. Preferably, the functionalization agent can be chosen from
 30 (3-cyanohexyl)trimethoxysilane, (3-cyanohexyl)triethoxysilane, (3-
 cyanohexyl)dimethoxymethylsilane and (3-
 cyanohexyl)diethoxymethylsilane.

[0066] The process which is a subject-matter of the invention comprises a first stage of polymerization of at least one conjugated diene monomer.

[0067] This polymerization stage according to the invention can be carried out by anionic polymerization initiated, for example, by means of an organic compound of an alkali metal or alkaline earth metal. According to other implementations of the process of the invention, this polymerization stage can be a chain polymerization by catalysis (according to the coordination-insertion mechanism), by means of a catalytic system based on a rare earth metal, on titanium or on another transition metal. The polymerization of at least one conjugated diene monomer according to these different implementations generates elastomer chains having a reactive site at the chain end. According to the polymerization method used, these sites are more or less reactive. The term then commonly used is (pseudo-)living elastomer or (pseudo-)living chain.

[0068] In the context of an anionic polymerization, the polymerization initiator can be any known mono- or polyfunctional anionic initiator. However, an initiator containing an alkali metal, such as lithium, or an alkaline earth metal, such as barium, is preferably used. An initiator containing an alkali metal, such as lithium, is preferably used. Those organolithium initiators comprising at least one carbon-lithium bond and at least one nitrogen-lithium bond are suitable in particular as organolithium initiators. Representative compounds are aliphatic organolithium compounds, such as ethyllithium, n-butyllithium (n-BuLi) or isobutyllithium, or lithium amides obtained from a cyclic secondary amine, such as pyrrolidine and hexamethyleneimine. Such anionic polymerization initiators are known to a person skilled in the art.

[0069] In the context of a chain polymerization by coordination catalysis, use is made of a catalytic system based on a rare earth metal, on titanium or on another transition metal. Such catalytic systems are fully described in the literature.

[0070] The polymerization can be carried out in a way known per se continuously. The polymerization is generally carried out at temperatures of between 0°C and 110°C and preferably from 60°C to 100°C, indeed even from 70°C to 90°C. The temperature can be kept constant throughout this stage or can be variable, according to the targeted characteristics of the elastomer synthesized. The polymerization process can be carried out in solution, in a more or less concentrated or dilute medium. The polymerization solvent is preferably an inert hydrocarbon solvent which can, for example, be an aliphatic or alicyclic hydrocarbon, such as pentane, hexane, heptane, isooctane, cyclohexane or methylcyclohexane, or an aromatic hydrocarbon, such as benzene, toluene or xylene.

[0071] Preferably, the polymerization is an anionic polymerization as it makes it possible to achieve a greater content of functionalized chains than that obtained with a polymerization by coordination catalysis. Thus, preferably, the process which is a subject-matter of the invention comprises a stage of anionic polymerization of at least one conjugated diene monomer in the presence of a polymerization initiator.

[0072] The following are suitable in particular as conjugated diene monomers: 1,3-butadiene, isoprene, 2,3-di(C₁-C₅ alkyl)-1,3-butadienes, such as, for example, 2,3-dimethyl-1,3-butadiene, 2,3-diethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-butadiene or 2-methyl-3-isopropyl-1,3-butadiene, an aryl-1,3-butadiene, 1,3-pentadiene or 2,4-hexadiene.

[0073] According to some alternative forms of the process of the invention, the conjugated diene monomer can be homopolymerized.

[0074] According to other alternative forms of the process of the invention, the conjugated diene monomer can be copolymerized with one or more conjugated diene monomers and/or with one or more ethylenically unsaturated monomers including aliphatic mono-olefins, such as ethylene and aliphatic α -olefins having from 3 to 18 carbon atoms, and vinylaromatic compounds having from 8 to 20 carbon atoms.

[0075] For example, an aliphatic α -olefin having from 3 to 18 carbon atoms, advantageously having from 3 to 6 carbon atoms, is suitable as aliphatic α -olefin monomer. Mention may be made of propylene, butene, pentene, hexene or a mixture of these compounds.

5 [0076] The following in particular are suitable as vinylaromatic monomers: styrene, ortho-, meta- or para-methylstyrene, α -methylstyrene, the "vinyltoluene" commercial mixture, para-(tert-butyl)styrene, methoxystyrenes, vinylmesitylene, divinylbenzene and vinylnaphthalene, and the like. Advantageously, the vinylaromatic monomer is styrene.

10 [0077] These alternative forms can be combined with the preferred or substitute alternative forms and aspects described below.

[0078] According to alternative forms of the invention, one or more compound(s) having an impact on the microstructure of the diene elastomer can be used, such as, for example, a modifying agent or a randomizing agent.
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[0079] The anionic polymerization of at least one conjugated diene monomer in the presence of a polymerization initiator, which is the preferred implementation of the polymerization in the context of the invention, generates elastomer chains having a reactive site at the chain end. The term then commonly used is living elastomer or living chain.
20 These living chains, or living elastomers, subsequently react with the reactive sites of at least one functionalization agent during the modification stage. The modification stage can take place in the presence of a functionalization agent corresponding to the Formula 2 or of a mixture of at least two different functionalization agents each corresponding to the Formula 2.
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[0080] The molar ratio of the functionalization agent to the metal of the polymerization initiator essentially depends on the type of modified diene elastomer desired. Thus, according to some alternative forms of the invention, with a molar ratio of the functionalization agent to the metal of the
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polymerization initiator of at least 0.30, in particular ranging from 0.30 to 0.65, preferably from 0.35 to 0.65 and more preferably still from 0.40 to 0.60, indeed even from 0.45 to 0.55, the formation of coupled elastomers within the modified elastomer is favoured. According to other alternative forms of the invention, with a ratio of greater than 0.50, particularly of greater than or equal to 0.65, preferably of greater than 1 or also varying from 0.65 to 1.45, elastomers functionalized at the chain end are predominantly formed.

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[0081] The process for the synthesis of the modified diene elastomer according to the invention can be continued in a way known per se by the stages of recovery of the modified elastomer.

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[0082] According to the alternative forms of the invention according to which the functionalization agent bears a protected primary or secondary amine functional group, the synthesis process can be continued by a stage of deprotection of the primary or secondary amine. This stage is carried out after the modification reaction. The chains functionalized by the protected amine group can, by way of example, be reacted with an acid, a base, a fluorinated derivative, such as tetrabutylammonium fluoride, a silver salt, such as silver nitrate, and the like, in order to deprotect this amine functional group. These different methods are described in the work "Protective Groups in Organic Synthesis", T. W. Green and P. G. M. Wuts, Third Edition, 1999. This deprotection stage can have the effect of hydrolysing all or a portion of the hydrolysable alkoxysilane functional groups of the modified diene elastomer in order to convert them into silanol functional groups.

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[0083] According to alternative forms of the invention, the synthesis process can comprise a stage of hydrolysis of the hydrolysable alkoxysilane functional groups by addition of an acidic, basic or neutral compound, as described in the document EP 2 266 819 A1. The hydrolysable functional groups are then converted into silanol functional groups.

[0084] The process for the synthesis of the modified diene elastomer according to the invention can be continued in a way known per se by the stages of recovery of the modified elastomer.

5 [0085] According to alternative forms of this process, these stages comprise a stripping stage for the purpose of recovering the elastomer resulting from the prior stages in dry form. This stripping stage can have the effect of hydrolysing all or a portion of the hydrolysable alkoxy silane functional groups of the modified diene elastomer in order to convert them into silanol functional groups. Advantageously, at least 50 mol% to 70 mol% of the
10 functional groups can thus be hydrolysed.

[0086] Another subject-matter of the invention is some of the functionalization agents of Formula 2 as novel compounds, including the preferred alternative forms and aspects described above. More particularly, a subject-matter of the invention is then, as novel compounds, the
15 functionalization agents of Formula 2 in which X represents a tertiary amine or protected or unprotected secondary amine functional group, an isocyanate functional group, an imine functional group or a cyano functional group. More particularly still, a subject-matter of the invention is then, as novel compounds, the functionalization agents of Formula 2 in which X
20 represents a tertiary amine or protected or unprotected secondary amine functional group, preferably a dialkylamino- tertiary amine functional group, the alkyl radicals of which, independently of one another, are C₁-C₄ alkyl radicals, preferably methyl or ethyl.

[0087] Another subject-matter of the invention is an elastomer directly
25 obtained by the synthesis process described above.

[0088] A further subject-matter of the invention is a rubber composition based on at least one reinforcing filler and on an elastomer matrix comprising at least one modified diene elastomer according to the invention.

[0089] The elastomer matrix can comprise up to 100 phr of modified diene elastomer according to the invention. In the context of the reinforced rubber composition, the term "modified diene elastomer according to the invention" is understood to mean not only a modified elastomer according to the invention but also any mixture of at least two modified elastomers according to the invention.

[0090] According to alternative forms of the invention, the elastomer matrix can also comprise at least one diene elastomer other than the said modified diene elastomer according to the invention. This or these diene elastomers other than the modified diene elastomer according to the invention can be chosen from the diene elastomers conventionally used in tyres, such as natural rubber or a synthetic elastomer, or also another functionalized, coupled or star-branched elastomer. This or these diene elastomers other than the said modified diene elastomer according to the invention can then be present from 1 to 70 parts by weight per 100 parts of modified diene elastomer according to the invention.

[0091] According to other alternative forms, the matrix is composed solely of this modified diene elastomer according to the present invention.

[0092] Use may be made, as reinforcing filler, of any type known for its abilities to reinforce a rubber composition which can be used in the manufacture of tyres, for example carbon black, a reinforcing inorganic filler, such as silica, with which is combined, in a known way, a coupling agent, or also a mixture of these two types of filler.

[0093] According to a particularly advantageous alternative form of the invention, the reinforcing filler is predominantly other than carbon black, that is to say that it comprises more than 50% by weight of the total weight of the filler of one or more fillers other than carbon black, in particular a reinforcing inorganic filler, such as silica; indeed it even consists exclusively of such a filler.

[0094] According to this other alternative form, when carbon black is also present, it can be used at a content of less than 20 phr, more preferably of less than 10 phr (for example, between 0.5 and 20 phr, in particular from 1 to 10 phr).

5 [0095] Preferably, the amount of reinforcing filler (carbon black and/or other reinforcing filler, such as silica) is between 10 and 200 phr, more preferably between 30 and 150 phr, the optimum being, in a known way, different according to the specific applications targeted.

10 [0096] All carbon blacks, used individually or in the form of mixtures, are suitable as carbon blacks, in particular the blacks conventionally employed in tyres or their treads ("tyre-grade" blacks). These carbon blacks can be used in the isolated state, as available commercially, or in any other form, for example as support for some of the rubber additives used.

15 [0097] Reinforcing inorganic filler should be understood here as meaning any other inorganic or mineral filler, whatever its colour and its origin (natural or synthetic), capable of reinforcing by itself alone, without means other than an intermediate coupling agent, a rubber composition intended for the manufacture of tyres; such a filler is generally characterized, in a known way, by the presence of hydroxyl groups at its surface.

20 [0098] Mineral fillers of the siliceous type, preferably silica (SiO_2), are suitable in particular as reinforcing inorganic fillers. The silica used can be any reinforcing silica known to a person skilled in the art, in particular any precipitated or fumed silica exhibiting a BET specific surface and also a CTAB specific surface both of less than $450 \text{ m}^2/\text{g}$, preferably from 30 to $400 \text{ m}^2/\text{g}$, in particular between 60 and $300 \text{ m}^2/\text{g}$. Mention will also be made of
25 mineral fillers of the aluminous type, in particular alumina (Al_2O_3) or aluminium (oxide) hydroxides, or also of reinforcing titanium oxides, for example described in US 6 610 261 and US 6 747 087. Reinforcing fillers of another nature, in particular carbon black, are also suitable as reinforcing
30 fillers, provided that these reinforcing fillers are covered with a siliceous

layer or else comprise, at their surface, functional sites, in particular hydroxyl sites, requiring the use of a coupling agent in order to form the connection between the filler and the elastomer. Mention may be made, by way of example, for example, of carbon blacks for tyres, such as described, for example, in Patent Documents WO 96/37547 and WO 99/28380.

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[0099] The physical state under which the reinforcing filler is provided is not important, whether it is in the form of a powder, of microbeads, of granules, or else of beads. Of course, reinforcing inorganic filler is also understood to mean mixtures of different reinforcing fillers, in particular of highly dispersible silicas as described above.

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[0100] When silica is present in the composition as reinforcing filler, use may be made, as coupling agents, of organosilanes, in particular alkoxysilane polysulfides or mercaptosilanes, or else of at least bifunctional polyorganosiloxanes. Silica/elastomer bonding agents, in particular, have been described in a large number of documents, the best known being bifunctional alkoxysilanes, such as alkoxysilane polysulfides.

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[0101] In the compositions in accordance with the invention, the amount of coupling agent is advantageously less than 20 phr, it being understood that it is generally desirable to use as little as possible of it. Its content is preferably between 0.5 and 12 phr. The presence of the coupling agent depends on the presence of the reinforcing inorganic filler. Its content is easily adjusted by a person skilled in the art according to the content of this filler; it is typically of the order of 0.5% to 15% by weight, with respect to the amount of reinforcing inorganic filler.

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[0102] The rubber compositions in accordance with the invention can also comprise, in addition to the coupling agents, coupling activators, agents for covering the fillers or more generally processing aids capable, in a known way, by virtue of an improvement in the dispersion of the filler in the rubber matrix and of a lowering of the viscosity of the compositions, of improving their ability to be processed in the raw state, these agents being, for

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example, hydrolysable silanes, such as alkylalkoxysilanes, polyols, polyethers, primary, secondary or tertiary amines, or hydroxylated or hydrolysable polyorganosiloxanes.

5 [0103] The rubber compositions in accordance with the invention can also comprise reinforcing organic fillers which can replace all or a portion of the carbon blacks or of the other reinforcing fillers described above. Mention may be made, as examples of reinforcing organic fillers, of functionalized polyvinyl organic fillers, such as described in Applications WO-A-2006/069792, WO-A-2006/069793, WO-A-2008/003434 and WO-A-10 2008/003435.

[0104] The rubber compositions in accordance with the invention can also comprise all or a portion of the normal additives customarily used in elastomer compositions intended for the manufacture of tyres, such as, for example, pigments, protective agents, such as anti-ozone waxes, chemical antiozonants or antioxidants, anti-fatigue agents, reinforcing or plasticizing resins, methylene acceptors (for example, phenolic novolak resin) or methylene donors (for example, HMT or H3M), such as described, for example, in Application WO 02/10269, a crosslinking system based either on sulfur or on sulfur donors and/or on peroxides and/or on bismaleimides, 15 vulcanization accelerators, vulcanization activators, promoters of adhesion to non-rubber surfaces, such as cobalt-based compounds, plasticizing agents, preferably non-aromatic or very slightly aromatic plasticizing agents selected from the group consisting of naphthenic oils, paraffinic oils, MES oils, TDAE oils, ether plasticizers, ester plasticizers, hydrocarbon resins 20 exhibiting a high Tg, preferably of greater than 30°C, such as described, for example, in Applications WO 2005/087859, WO 2006/061064 and WO 2007/017060, and the mixtures of such compounds.

25 [0105] Another subject-matter of the invention is a process for the preparation of a rubber composition as described above.

[0106] The composition is manufactured in appropriate mixers, using two successive phases of preparation well known to a person skilled in the art: a first phase of thermomechanical working or kneading ("non-productive" phase) at high temperature, up to a maximum temperature of between 110°C and 190°C, preferably between 130°C and 180°C, followed by a second phase of mechanical working ("productive" phase) down to a lower temperature, typically of less than 110°C, for example between 40°C and 100°C, during which finishing phase the crosslinking system is incorporated.

[0107] The process in accordance with the invention for preparing a rubber composition according to the invention comprises at least the following stages:

- carrying out, at a maximum temperature of between 110°C and 190°C, preferably between 130°C and 180°C, a first step of thermomechanical working (sometimes described as "non-productive" phase) of the base constituents necessary for the rubber composition, with the exception of the crosslinking system and, if appropriate, an adhesion promoter, by intimately incorporating, by kneading in one or more stages, ingredients of the composition in the elastomer matrix comprising the modified diene elastomer according to the invention, then
- carrying out, at a temperature lower than the said maximum temperature of the said first step, preferably of less than 110°C, a second step of mechanical working during which the said crosslinking system and, if appropriate, an adhesion promoter are incorporated.

[0108] According to alternative forms of the invention, the process for the preparation of the rubber composition comprises the stages of preparation of the modified diene elastomer according to the invention as described above according to its different methods of synthesis.

[0109] The final composition thus obtained can subsequently be calendered, for example in the form of a sheet or of a plaque, or also extruded, for example in order to form a rubber profiled element which can be used as semi-finished product made of rubber intended for the tyre.

5 [0110] Another subject-matter of the invention is a semi-finished product made of rubber comprising a rubber composition according to the invention.

[0111] Another subject-matter of the invention is a tyre, at least one of its constituent elements of which is a semi-finished product made of rubber comprising a rubber composition according to the invention.

10 [0112] Due to the improvement in the hysteresis/processing compromise which characterizes a rubber composition based on a modified elastomer comprising an alkoxysilane functional group and a functional group comprising a nitrogen atom, it should be noted that such a composition can constitute any semi-finished product of the tyre and very particularly the
15 tread, thus reducing the rolling resistance of the tyre.

[0113] A better understanding of the abovementioned characteristics of the present invention, and also others, will be obtained on reading the following description of several implementational examples of the invention, given by way of illustration and without limitation.

20

Examples

Measurement used

High-resolution size exclusion chromatography (HR SEC)

25 The high-resolution SEC technique is used to determine the percentages by weight of the various populations of chains present in a polymer sample (1 branch (1b), 2 branches (2b), 3 branches (3b), 4 branches (4b)).

There is no specific treatment of the polymer sample before analysis. The latter is simply dissolved in the elution solvent at a concentration of approximately 1 g.l^{-1} . The solution is then filtered through a filter with a porosity of $0.45 \text{ }\mu\text{m}$ before injection.

- 5 The apparatus used is a Waters Alliance 2695 chromatographic line. The elution solvent is tetrahydrofuran, the flow rate is 0.2 ml.min^{-1} and the temperature of the system is 35°C . A set of three identical columns in series is used (Shodex, length 300 mm , diameter 8 mm). The number of theoretical plates of the set of columns is greater than $22\,000$. The volume of the solution of the polymer sample injected is
10 $50 \text{ }\mu\text{l}$. The detector is a Waters 2414 differential refractometer and the software for making use of the chromatographic data is the Waters Empower system.

The calculated molar masses are relative to a calibration curve produced for SBRs having the following microstructure: 25% by weight of units of styrene type, 23% by weight of units of 1,2- type and 50% by weight of units of trans-1,4- type.

15 Examples of preparation of elastomers

- 94.0 ml (72.4 g) of methylcyclohexane, 11.6 ml (7.5 g) of butadiene, 2.5 ml (2.3 g) of styrene and 0.78 ml of a 0.73 mol.l^{-1} solution of tetrahydrofuran in methylcyclohexane are introduced into two 250 ml glass bottles (Steinie bottles). After neutralization of the impurities in the solution to be polymerized by addition of
20 n-butyllithium (n-BuLi), 0.52 ml of 0.111 mol.l^{-1} n-BuLi in methylcyclohexane are added. The polymerization is carried out at 50°C .

After 50 minutes, the degree of conversion of monomers reaches 70%. This content is determined by weighing an extract dried at 140°C under a reduced pressure of 200 mmHg .

- 25 0.75 ml of a 0.05 mol.l^{-1} solution of (3-N,N-dimethylaminopropyl)trimethoxysilane in methylcyclohexane is added to the solution of living polymer (0.65 molar eq. vs Li) present in bottle N° 1 and 0.76 ml of a 0.049 mol.l^{-1} solution of (6-N,N-dimethylaminohexyl)trimethoxysilane in methylcyclohexane is added to the solution of living polymer (0.65 molar eq. vs Li) present in bottle N° 2. After

reacting for 15 minutes at 60°C, 1 ml of pure methanol is added to bottles 1 and 2 and then 1 ml of a solution containing an 80/20 g/l mixture of antioxidants 4,4'-methylenebis(2,6-di(tert-butyl)phenol)/N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine in toluene is added to bottles 1 and 2. The polymers thus
5 treated are separated from their solution by drying at 60°C under reduced pressure and a nitrogen stream for 12 hours.

HR SEC analyses are carried out on the finished product recovered on conclusion of this drying stage (Day D) and then after storing the elastomers at ambient temperature and in ambient air for 7 days and then 30 days (respectively D+7 and
10 D+30).

The results are presented in Table 1.

Table 1

Sample	Functionalization agent	HR SEC D finished product (%1b/2b/3b/4b)	HR SEC D + 7 (%1b/2b/3b/4b)	HR SEC D + 30 (%1b/2b/3b/4b)
1 (comparative)	(A)	54/41/3/2	29/46/16/9	22/38/27/13
2 (invention)	(B)	66/34/0/0	64/35/1/0	64/35/1/0

(A): (3-N,N-dimethylaminopropyl)trimethoxysilane

(B): (6-N,N-dimethylaminohexyl)trimethoxysilane

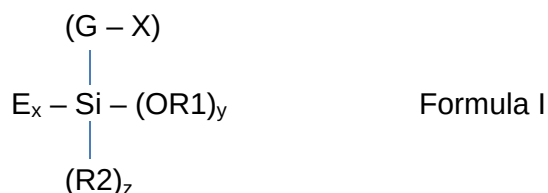
It is apparent, from the results presented in Table 1, that the elastomer 2 according to the invention, obtained by functionalization with (6-N,N-dimethylaminohexyl)trimethoxysilane, exhibits a distribution of the populations comprising 1, 2 and 3 branches which is stable on storage, unlike the comparative elastomer 1, obtained with (3-N,N-dimethylaminopropyl)trimethoxysilane, which exhibits a strong change in the distribution of the populations on storage.

CLAIMS

- 5 1. Modified diene elastomer comprising, within the main chain of the elastomer, a silicon atom substituted, on the one hand, by at least one alkoxy group, optionally partially or completely hydrolysed to give a hydroxyl group, and, on the other hand, by at least one other functional group comprising a nitrogen atom bonded to the silicon atom via a spacer group chosen from saturated linear divalent aliphatic hydrocarbon radicals having

10 at least 5 carbon atoms, preferably at least 6, and at most 10 carbon atoms, preferably at most 9.
2. Modified diene elastomer according to Claim 1, characterized in that the diene elastomer is a homopolymer of a diene monomer or a copolymer of at least one diene monomer and a vinylaromatic monomer.
- 15 3. Modified diene elastomer according to Claim 2, characterized in that the diene monomer is butadiene or isoprene.
4. Modified diene elastomer according to Claim 2 or 3, characterized in that the vinylaromatic monomer is styrene.
- 20 5. Modified diene elastomer according to any one of the preceding claims, characterized in that the spacer group is a saturated linear divalent C₆, C₇, C₈ or C₉, preferably C₆, aliphatic hydrocarbon radical.
- 25 6. Modified diene elastomer according to any one of the preceding claims, characterized in that the other functional group is a cyclic or non-cyclic, tertiary, protected or unprotected secondary or protected or unprotected primary amine, an isocyanate, an imine or a cyano.
7. Modified diene elastomer according to Claim 6, characterized in that the other functional group is a dialkylamino- tertiary amine, the alkyl radicals of which, independently of one another, are C₁-C₄ alkyl radicals, preferably methyl or ethyl.

8. Modified diene elastomer according to any one of the preceding claims, characterized in that it corresponds to the following general formula I:



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in which:

- E represents the diene elastomer chain;
- R1 represents a hydrogen atom or a C₁-C₁₀, indeed even C₁-C₈, alkyl radical, preferably a C₁-C₄ alkyl radical, more preferably methyl and ethyl;
- R2 represents a substituted or unsubstituted C₁-C₁₀, indeed even C₁-C₈, alkyl radical, preferably a C₁-C₄ alkyl radical, more preferably methyl and ethyl;
- G represents the spacer group chosen from saturated linear divalent C₆, C₇, C₈ or C₉, preferably C₆, aliphatic hydrocarbon radicals;
- X represents the functional group comprising a nitrogen atom;
- x has the value 1 or 2, y has the value 1 or 2 and z has the value 0 or 1, with the proviso that x + y + z = 3.

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9. Modified diene elastomer according to Claim 8, characterized in that y has the value 1.

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10. Modified diene elastomer according to Claim 9, characterized in that x = z = 1.

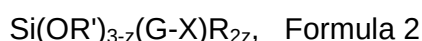
11. Modified diene elastomer according to Claim 9, characterized in that x = 2 and z = 0.

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12. Process for the synthesis of a modified diene elastomer comprising, within the main chain of the elastomer, a silicon atom substituted, on the one hand, by at least one alkoxy group, optionally partially or completely

hydrolysed to give a hydroxyl group, and, on the other hand, by at least one other functional group comprising a nitrogen atom bonded to the silicon atom via a spacer group, characterized in that it comprises:

- a) a stage of polymerization of at least one diene monomer,
- 5 b) a stage of modification of the living diene elastomer obtained in the preceding stage by means of at least one functionalization agent corresponding to the following general formula:



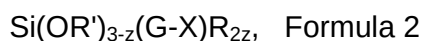
in which:

- 10 - G is a spacer group chosen from saturated linear divalent aliphatic hydrocarbon radicals having at least 5 carbon atoms, preferably at least 6, and at most 10 carbon atoms, preferably at most 9;
- X represents a functional group comprising a nitrogen atom;
- R', independently of one another, represent a C₁-C₁₀, indeed even
15 C₁-C₈, alkyl group, preferably a C₁-C₄ alkyl group, more preferably methyl and ethyl;
- R₂ represents a C₁-C₁₀, indeed even C₁-C₈, alkyl group, more preferably methyl and ethyl;
- z has the value 0 or 1.

- 20 13. Process according to Claim 12, characterized in that the functional group X is a cyclic or non-cyclic, tertiary, protected or unprotected secondary or protected or unprotected primary amine, an isocyanate, an imine, a cyano, preferably a dialkylamino- tertiary amine, the alkyl radicals of which, independently of one another, are C₁-C₄ alkyl radicals, preferably methyl or
25 ethyl.

14. Process according to Claim 12 or 13, characterized in that the spacer group is a saturated linear divalent C₆, C₇, C₈ or C₉, preferably C₆, aliphatic hydrocarbon radical.

15. Process according to any one of Claims 12 to 14, characterized in that $z = 0$.
16. Process according to any one of Claims 12 to 14, characterized in that $z = 1$.
- 5 17. Process according to any one of Claims 12 to 16, characterized in that the polymerization stage is carried out by anionic polymerization in the presence of a polymerization initiator.
- 10 18. Process according to Claim 17, characterized in that the molar ratio of the functionalization agent to the metal of the polymerization initiator is greater than 0.5 and preferably greater than 0.65.
19. Process according to Claim 17, characterized in that the molar ratio of the functionalization agent to the metal of the polymerization initiator varies from 0.35 to 0.65, preferably from 0.40 to 0.60.
- 15 20. Process according to any one of Claims 12 to 19, characterized in that the diene monomer is butadiene or isoprene.
21. Process according to any one of Claims 12 to 20, characterized in that the polymerization stage is a stage of copolymerization of at least one diene monomer and an ethylenically unsaturated monomer.
- 20 22. Process according to Claim 21, characterized in that the ethylenically unsaturated monomer is a vinylaromatic monomer, preferably styrene.
23. Modified diene elastomer obtained by the process according to any one of Claims 12 to 22.
- 25 24. Rubber composition based on at least one reinforcing filler and an elastomer matrix comprising a modified diene elastomer as described in any one of Claims 1 to 11 and 23.
25. Tyre comprising a rubber composition according to Claim 24.
26. Compound corresponding to the following general formula:



in which:

- G is a spacer group chosen from saturated linear divalent aliphatic hydrocarbon radicals having at least 5 carbon atoms, preferably at least 6, and at most 10 carbon atoms, preferably at most 9;
 - X represents a tertiary amine or protected or unprotected secondary amine functional group, an isocyanate functional group, an imine functional group or a cyano functional group;
 - R', independently of one another, represent a C₁-C₁₀, indeed even C₁-C₈, alkyl group, preferably a C₁-C₄ alkyl group, more preferably methyl and ethyl;
 - R₂ represents a C₁-C₁₀, indeed even C₁-C₈, alkyl group, more preferably methyl and ethyl;
 - z has the value 0 or 1.
27. Compound according to Claim 26, characterized in that the spacer group is a saturated linear divalent C₆, C₇, C₈ or C₉, preferably C₆, aliphatic hydrocarbon radical.
28. Compound according to Claim 26 or 27, characterized in that the functional group X is a tertiary or protected or unprotected secondary amine, preferably a dialkylamino- tertiary amine, the alkyl radicals of which, independently of one another, are C₁-C₄ alkyl radicals, preferably methyl or ethyl.