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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 January 2019 (24.01.2019)

(10) International Publication Number
WO 2019/016885 A1

(51) International Patent Classification:
C08L 15/00 (2006.01) *C08L 9/00* (2006.01)
B60C 1/00 (2006.01) *C08L 83/06* (2006.01)
C08K 3/00 (2006.01)

(21) International Application Number:
PCT/JP2017/026083

(22) International Filing Date:
19 July 2017 (19.07.2017)

(25) Filing Language: English

(26) Publication Language: English

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

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

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

WO 2019/016885 A1

(54) Title: A RUBBER COMPOSITION BASED ON SILICONE OIL

(57) Abstract: A rubber composition, which can allow improving a balance of performances between low strain stiffness and hysteresis, is based on at least an elastomer matrix comprising 20 to 100 phr of a first diene elastomer bearing at least one SiOR function, R being a hydrogen atom or a hydrocarbon radical, and optionally, 0 to 80 phr of a second diene elastomer which is different from the first diene elastomer; a reinforcing filler comprising at least 60 phr of a reinforcing inorganic filler; and a plasticizing agent comprising more than 4 phr of a mercapto-modified silicone oil.

Description

Title of Invention: A RUBBER COMPOSITION BASED ON SILICONE OIL

Technical Field

[0001] The field of the invention is that of rubber compositions for tires, more precisely rubber compositions for tire treads.

Background Art

[0002]

Citation List

Patent Literature

[0003] PTL 1: WO2013/087878

[0004] It is known to use, in some parts of the tires, rubber compositions exhibiting a high stiffness during small strains (cf. the patent literature 1). Resistance to small strains corresponds to road behaviors, which is an important feature of the tires.

[0005] This stiffening can be obtained by increasing the content of reinforcing filler or by incorporating certain reinforcing resins in the constituent rubber compositions of the parts of the tire.

[0006] However, in a known way, the increase in the stiffness of a rubber composition by increasing the content of filler can be disadvantageous to the hysteresis properties and thus rolling resistance properties of the tires. Therefore, it is an ongoing aim to lower the rolling resistance of tires in order to reduce the consumption of fuel, for economic and environmental purposes.

Summary of Invention

Technical Problem

[0007] During their research, the inventor has discovered a specific rubber composition which allows an unexpectedly improved balance of performances between road behavior and rolling resistance of a tire.

[0008] In the present description, unless expressly stated otherwise, all the percentages (%) indicated are percentages by weight (wt%).

[0009] The expression “elastomer matrix” is understood to mean, in a given composition, all of the elastomers present in said rubber composition.

[0010] The abbreviation “phr” signifies parts by weight per hundred parts by weight of the elastomer matrix in the considered rubber composition.

[0011] In the present description, unless expressly indicated otherwise, each Tg_{DSC} (glass transition temperature) is measured in a known way by DSC (Differential Scanning

Calorimetry) in accordance with Standard ASTM D3418-08.

[0012] Any interval of values denoted by the expression “between a and b” represents the range of values of greater than “a” and of less than “b” (i.e. the limits a and b excluded) whereas any interval of values denoted by the expression “from a to b” means the range of values going from “a” to “b” (i.e. including the strict limits a and b).

[0013] The expression “based on” should be understood in the present application to mean a composition comprising the mixture(s) and/or the product of the reaction of the various constituents used, some of the constituents being able or intended to react together, at least partly, during the various manufacturing phases of the composition, in particular during the vulcanization (curing).

Solution to Problem

[0014] A first aspect of the invention is a rubber composition based on at least an elastomer matrix comprising 10 to 100 phr of a first diene elastomer bearing at least one SiOR function, R being a hydrogen atom or a hydrocarbon radical, and optionally, 0 to 90 phr of a second diene elastomer which is different from the first diene elastomer, which means comprising no second diene elastomer or at most 90 phr of the second diene elastomer; a reinforcing filler comprising at least 60 phr of a reinforcing inorganic filler; and a plasticizing agent comprising more than 4 phr of a mercapto-modified silicone oil.

Advantageous Effects of Invention

[0015] The specific rubber composition allows improving the balance of performances between road behavior and rolling resistance of the tire as represented by low strain stiffness and hysteresis.

[0016] Each of the below aspect(s), the embodiment(s) and the variant(s) including each of the preferred range(s) and/or matter(s) may be applied to any one of the other aspect(s), the other embodiment(s) and the other variant(s) of the invention unless expressly stated otherwise.

[0017] Elastomer (or loosely “rubber”, the two terms being regarded as synonyms) of the “diene” type is to be understood in a known manner as an (meaning one or more) elastomer derived at least partly (i.e. a homopolymer or a copolymer) from diene monomers (monomers bearing two carbon-carbon double bonds, conjugated or not).

[0018] These diene elastomers can be classified into two categories: “essentially unsaturated” or “essentially saturated”. Generally, the expression “essentially unsaturated” is understood to mean a diene elastomer resulting at least in part from conjugated diene monomers having a content of units of diene origin (conjugated dienes) which is greater than 15% (mol %); thus it is that diene elastomers such as butyl rubbers or diene/α -olefin copolymers of the EPDM type do not fall under the preceding definition and may especially be described as “essentially saturated” diene elastomers (low or very low content of units of diene origin, always less than 15%). In the category of “essentially unsaturated” diene elastomers, the expression “highly unsaturated” diene elastomer is understood to mean in particular a diene elastomer having a content of units of diene origin (conjugated dienes) which is greater than 50%.

[0019] Although it applies to any type of diene elastomer, a person skilled in the art of tires will understand that the invention is preferably employed with essentially unsaturated diene elastomers.

[0020] Given these definitions, the expression diene elastomer capable of being used in the compositions in accordance with the invention is understood in particular to mean:

(a) - any homopolymer obtained by polymerization of a conjugated diene monomer, preferably having from 4 to 12 carbon atoms;

(b) - any copolymer obtained by copolymerization of one or more conjugated dienes with one another or with one or more vinyl aromatic compounds preferably having from 8 to 20 carbon atoms.

[0021] The following are suitable in particular as conjugated dienes: 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-di(C_1-C_5 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. The following, for example, are suitable as vinylaromatic compounds: styrene, ortho-, meta- or para-methylstyrene, the“vinyltoluene” commercial mixture, para-(tert-butyl) styrene, methoxystyrenes, chlorostyrenes, vinylmesitylene, divinylbenzene or vinylnaphthalene.

[0022] The first diene elastomer may be selected from the group consisting of polybutadienes (BRs), synthetic polyisoprenes (IRs), natural rubber (NR), butadiene copolymers, isoprene copolymers and the mixtures thereof; such copolymers are selected more preferably from the group consisting of butadiene-styrene copolymers (SBRs) and the mixtures thereof.

[0023] The first diene elastomer may have any microstructure which depends on the polymerization conditions used, in particular on the presence or absence of a modifying and/or randomizing agent and on the amounts of modifying and/or randomizing agent employed. This elastomer may, for example, be a block, statistical, sequential or micro sequential elastomer and may be prepared in dispersion or in solution.

[0024] The first diene elastomer bears at least one SiOR function, R being a hydrogen atom or a hydrocarbon radical.

[0025] The expression “hydrocarbon radical” means a monovalent group essentially consisting of carbon and hydrogen atoms. Such a group may comprise at least one heteroatom, and it is known that the assembly formed by the carbon and hydrogen atoms represents the major number fraction in the hydrocarbon radical, for example alkyl or alkoxyalkyl; preferably assembly formed by the carbon and hydrogen atoms represents the entirety of the hydrocarbon radical(s), for example alkyl. Such a SiOR (R is alkyl or alkoxyalkyl) is referred as an "alkoxysilane" function. While, a SiOH (R is a hydrogen atom) is referred as a "silanol" function.

[0026] Generally, a function borne by an elastomer, particularly a diene elastomer, may be located on the elastomer chain end(s) or may not be located at the elastomer chain ends, that is, may be away from the chain ends. The first case occurs for example when the diene elastomer is prepared using a polymerization initiator bearing the function or using a functionalizing agent. The second case occurs for example when the diene elastomer is modified by the use of a coupling agent or star-branching agent bearing the function.

[0027] A second aspect of the invention is the rubber composition according to the first aspect, wherein the first diene elastomer is a styrene-butadiene copolymer (SBR), preferably a solution styrene-butadiene copolymer which is a copolymer of butadiene and styrene, prepared in solution.

[0028] A third aspect of the invention is the rubber composition according to the first or the second aspect, wherein the SiOR function is located at the chain end of the first diene elastomer.

[0029] According to a preferred embodiment of the third aspect, the first diene elastomer bearing the SiOR function located at the chain end may be prepared according to the procedure described in a patent EP 0 778 311 B1, for example by reaction of the carbanion at the end of the living elastomeric chain with hexamethylcyclotrisiloxane followed by reaction with a proton donor.

[0030] A fourth aspect of the invention is the rubber composition according to the first or the second aspect, wherein the SiOR function is not located at the chain ends of the first diene elastomer.

[0031] According to a first variant of the fourth aspect, the SiOR function borne by the first diene elastomer may be a pendant group, which is equivalent to saying that the silicon atom of the SiOR function may not be inserted between the carbon-carbon bonds of the elastomer chain of the first diene elastomer. A diene elastomer bearing a pendant SiOR function may for example be prepared by hydrosilylation of the elastomer chain by a silane bearing an alkoxysilane group, followed by hydrolysis of the alkoxysilane function to give a SiOR function.

[0032] According to a second variant of the fourth aspect, the SiOR function borne by the first diene elastomer may not be a pendant group, but may be situated in the elastomer chain, that is, may be within the elastomer chain, which is equivalent to saying that the silicon atom of the SiOR function may be inserted between the carbon-carbon bonds of the elastomer chain of the first diene elastomer. Such a diene elastomer may be prepared according to the procedure described in a patent EP 2 285 852 B1. This second variant is preferential and applies to the fourth aspect.

[0033] A fifth aspect of the invention is the rubber composition according to any one of the first to the fourth aspects, wherein the first diene elastomer further bears at least one amine function, preferably at least one tertiary amine function.

[0034] According to a preferred embodiment of the fifth aspect, the amine function borne by the first diene elastomer may be a tertiary amine function. Mention will be made, as tertiary amine function, of the amines substituted with C_1-C_{10} alkyl radicals, preferably C_1-C_4 alkyl, more preferably methyl or ethyl radical(s).

[0035] According to this embodiment or a preferred embodiment of the fifth aspect, the amine function borne by the first diene elastomer may be a pendant group. The pendant position of the amine function means, in a known way, that the nitrogen atom of the amine function may not be inserted between the carbon-carbon bonds of the elastomer chain of the first diene elastomer.

[0036] A six aspect of the invention is the rubber composition according to the fifth aspects, wherein the SiOR function bears the amine function.

[0037] Such a diene elastomer may result from the modification of a diene elastomer by a coupling agent that introduces, the elastomer chain, an alkoxysilane group bearing an amine function according to the operating procedure described in a patent EP 2 285 852 B1. The following are suitable for example as coupling agent: N,N-dialkylaminopropyltrialkoxysilanes, C_1-C_{10}, preferably C_1-C_4, dialkyl groups, the compounds 3-(N,N-dimethylaminopropyl)trimethoxysilane, 3-(N,N-dimethylaminopropyl)triethoxysilane, 3-(N,N-diethylaminopropyl)trimethoxysilane, 3-(N,N-diethylaminopropyl)triethoxysilane being most particularly preferred, irrespective of the embodiment of the invention.

[0038] A seventh aspect of the invention is the rubber composition according to any one of the first to the sixth aspects, wherein R of the SiOR function is a hydrogen atom.

[0039] An eight aspect of the invention is the rubber composition according to any one of the first to the six aspects, wherein R of the SiOR function is a hydrocarbon radical.

[0040] According to a preferred embodiment of the eight aspect, the hydrocarbon radical may be an alkyl radical, preferably an alkyl radical having 1 to 12 carbon atoms, more preferably a branched, linear or else cyclic alkyl radical having 1 to 12 carbon atoms, still more preferably 1 to 6 carbon atoms, particularly 1 to 4 carbon atoms, more particularly methyl or ethyl radical(s).

[0041] A ninth aspect of the invention is the rubber composition according to any one of the first to the eighth aspects, wherein the first diene elastomer has a glass transition temperature (Tg_{DSC}) of lower than -40°C, (notably between -100°C and -40°C), advantageously less than -45°C (notably between -90°C and -45°C).

[0042] According to a preferred embodiment of the invention, the elastomer matrix may comprise 20 to 100 phr, preferably 30 to 100 phr, more preferably 40 to 100 phr, still more preferably 50 to 100 phr, particularly 60 to 100 phr, more particularly 70 to 100 phr, still more particularly 70 to 90 phr, of the first diene elastomer and 0 to 80 phr, preferably 0 to 70 phr, more preferably 0 to 60 phr, still more preferably 0 to 50 phr, particularly 0 to 40 phr, more particularly 0 to 30 phr, still more particularly 10 to 30 phr, of the second diene elastomer.

[0043] According to a preferred embodiment of the invention, the elastomer matrix may comprise 10 to 90 phr, preferably 10 to 80 phr, more preferably 10 to 70 phr, still more preferably 10 to 60 phr, particularly 10 to 50 phr, more particularly 10 to 40 phr, still more particularly 10 to 30 phr, of the first diene elastomer and 10 to 90 phr, preferably 20 to 90 phr, more preferably 30 to 90 phr, still more preferably 40 to 90 phr, particularly 50 to 90 phr, more particularly 60 to 90 phr, still more particularly 70 to 90 phr, of the second diene elastomer.

[0044] A tenth aspect of the invention is the rubber composition according to any one of the first to the ninth aspects, wherein the second diene elastomer is selected from the group consisting of polybutadienes, natural rubber, synthetic polyisoprenes, butadiene copolymers, isoprene copolymers and the mixtures thereof.

[0045] An eleventh aspect of the invention is the rubber composition according to the tenth aspect, wherein the second diene elastomer is polybutadienes.

[0046] The rubber composition according to the invention is based on a reinforcing filler.

[0047] The reinforcing filler may comprise a reinforcing inorganic filler (for instance, silica), carbon black or the mixtures thereof.

[0048] The reinforcing filler in the rubber composition according to the invention comprise at least 60 phr, preferably at least 70 phr, more preferably at least 80 phr, still more preferably at least 90 phr, particularly at least 100 phr, of a reinforcing inorganic filler.

[0049] A twelfth aspect of the invention is the rubber composition according to any one of the first to the eleventh aspects, wherein the reinforcing filler comprises 60 to 200 phr, preferably 70 to 180 phr, more preferably 80 to 160 phr, still more preferably at least 90 to 140 phr, particularly 100 to 120 phr, of a reinforcing inorganic filler.

[0050] The expression “reinforcing inorganic filler” should be understood here to mean any inorganic or mineral filler, whatever its color and its origin (natural or synthetic), also referred to as “white filler”, “clear filler” or even “non-black filler”, in contrast to carbon black, capable of reinforcing by itself alone, without means other than an intermediate coupling agent, a rubber composition intended for the manufacture of tires, in other words capable of replacing, in its reinforcing role, a conventional tire-grade carbon black; such a filler is generally characterized, in a known manner, by the presence of hydroxyl (-OH) groups at its surface.

[0051] The physical state under the presence of this filler is unimportant, whether it is in the form of powder, microbeads, granules, beads or any other suitable densified form. Of course, the reinforcing inorganic filler of the mixtures of various reinforcing inorganic fillers, preferably of highly dispersible siliceous and/or aluminous fillers is described hereafter.

[0052] Mineral fillers of the siliceous type, preferably silica (SiO_2) and/or the aluminous type, preferably alumina (Al_2O_3) are suitable in particular as the reinforcing inorganic fillers.

[0053] A thirteenth aspect of the invention is the rubber composition according to any one of the first to the twelfth aspects, wherein the reinforcing inorganic filler predominately comprises silica, that is, the reinforcing inorganic filler comprises more than 50% by weight of silica per 100% by weight of the reinforcing inorganic filler. Preferably, the reinforcing inorganic filler may comprise 100% by weight, of silica per 100% by weight of the reinforcing inorganic filler. The second rubber compositions may be based on a type of silica or a blend of several silicas. The silica used may be any reinforcing silica known to a person skilled in the art, in particular any precipitated or pyrogenic silica having a BET surface area and a CTAB specific surface area that are both less than 450 m^2/g, preferably from 20 to 400 m^2/g. Such silica may be covered or not. Mention will be made, as low specific surface silica, of Sidistar R300 from Elkem Silicon Materials. Mention will be made, as highly dispersible precipitated silicas (“HDSs”), for example, of “Ultrasil 7000” and “Ultrasil 7005” from Evonik, “Zeosil 1165 MP”, “Zeosil 1135 MP” and “Zeosil 1115 MP” from Rhodia, “Hi-Sil EZ150G” from PPG, “Zeopol 8715”, “Zeopol 8745” and “Zeopol 8755” from Huber or the silicas with a high specific surface area as described in a patent application WO 03/016387. Mention will be made, as pyrogenic silicas, for example, of “CAB-O-SIL S-17D” from Cabot, “HDK T40” from Wacker, “Aeroperl 300/30”, “Aerosil 380”, “Aerosil 150” or “Aerosil 90” from Evonik. Such silica may be covered, for example, “CAB-O-SIL TS-530” covered with hexamethyldiasilazene or “CAB-O-SIL TS-622” covered with dimethyldichlorosilane from Cabot.

[0054] The reinforcing inorganic filler used, particularly in case of that it is silica, has a BET surface area and a CTAB specific surface area that are advantageously 50 to 350 m^2/g, more advantageously 100 to 300 m^2/g, still more preferably between 150 and 250 m^2/g.

[0055] The BET surface area is measured according to a known method, that is, by gas adsorption using the Brunauer-Emmett-Teller method described in “The Journal of the American Chemical Society”, Vol. 60, page 309, February 1938, and more specifically, in accordance with the French standard NF ISO 9277 of December 1996 (multipoint volumetric method (5 points); where gas: nitrogen, degassing: 1 hour at 160°C, relative pressure range p/po: 0.05 to 0.17). The CTAB specific surface area is determined according to the French standard NF T 45-007 of November 1987 (method B).

[0056] A person skilled in the art will understand that a reinforcing filler of another nature, in particular organic nature, such as carbon black, might be used as filler equivalent to the reinforcing inorganic filler described in the present section, provided that this reinforcing filler is covered with an inorganic layer, such as silica, or else comprises, at its surface, functional sites, in particular hydroxyls, requiring the use of a coupling agent in order to form the connection between the filler and the elastomer. By way of example, mention may be made of carbon blacks for tires, such as described in patent applications WO 96/37547 and WO 99/28380.

[0057] A fourteenth aspect of the invention is the rubber composition according to any one of the first to the thirteenth aspects, wherein the reinforcing filler comprises less than 40 phr (for example, between 0.5 and 40 phr), preferably less than 30 phr (for example, between 1.0 and 30 phr), more preferably less than 20 phr (for example, between 1.5 and 20 phr), still more preferably less than 10 phr (for example, between 2 and 10 phr), of carbon black.

[0058] Within the ranges indicated, there is a benefit of coloring properties (black pigmentation agent) and anti-UV properties of carbon blacks, without furthermore adversely affecting the typical performance provided by the reinforcing inorganic filler, namely low hysteresis (reduced rolling resistance).

[0059] In order to couple the reinforcing inorganic filler to the elastomer matrix, for instance, the diene elastomer, use can be made, in a known manner, of a coupling agent (or bonding agent) intended to provide a satisfactory connection, of chemical and/or physical nature, between the reinforcing inorganic filler (surface of its particles) and the elastomer matrix, for instance, the diene elastomer. This coupling agent is at least bifunctional. Use can be made in particular of at least bifunctional organosilanes or polyorganosiloxanes.

[0060] Use can be made in particular of silane polysulphides, referred to as “symmetrical” or “asymmetrical” depending on their particular structure, as described, for example, in applications WO 03/002648, WO 03/002649 and WO 2004/033548.

[0061] Particularly suitable silane polysulphides correspond to the following general formula (I):

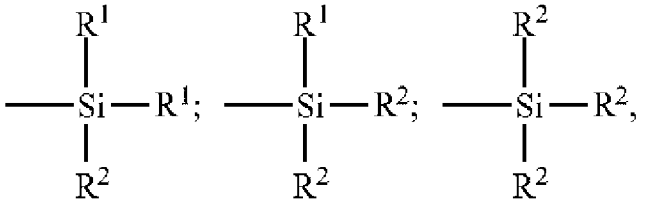
(I) Z - A - Sx - A - Z , in which:

- x is an integer from 2 to 8 (preferably from 2 to 5);
- A is a divalent hydrocarbon radical (preferably, C_1-C_{18} alkylene groups or C_6-C_{12}

arylene groups, more particularly C_1-C_{10}, in particular C_1-C_4, alkylenes, especially propylene);

- Z corresponds to one of the formulae below:

[Chem.1]



$$-\underset{R^2}{\overset{R^1}{\underset{|}{\overset{|}{Si}}}}-R^1;\quad -\underset{R^2}{\overset{R^1}{\underset{|}{\overset{|}{Si}}}}-R^2;\quad -\underset{R^2}{\overset{R^2}{\underset{|}{\overset{|}{Si}}}}-R^2,$$

in which:

- the R^1 radicals which are unsubstituted or substituted and identical to or different from one another, represent a C_1-C_{18} alkyl, C_5-C_{18} cycloalkyl or C_6-C_{18} aryl group (preferably, C_1-C_6 alkyl, cyclohexyl or phenyl groups, in particular C_1-C_4 alkyl groups, more particularly methyl and/or ethyl),

- the R^2 radicals which are unsubstituted or substituted and identical to or different from one another, represent a C_1-C_{18} alkoxyl or C_5-C_{18} cycloalkoxyl group (preferably a group selected from C_1-C_8 alkoxyls and C_5-C_8 cycloalkoxyls, more preferably a group selected from C_1-C_4 alkoxyls, in particular methoxyl and ethoxyl), are suitable in particular, without limitation of the above definition.

[0062] In the case of a mixture of alkoxysilane polysulphides corresponding to the above formula (I), in particular normal commercially available mixtures, the mean value of the "x" indices is a fractional number preferably of between 2 and 5, more preferably of approximately 4. However, the present invention can also advantageously be carried out, for example, with alkoxysilane disulphides (x = 2).

[0063] Mention will more particularly be made, as examples of silane polysulphides, of bis((C_1-C_4)alkoxyl(C_1-C_4)alkylsilyl(C_1-C_4)alkyl)polysulphides (in particular disulphides, trisulphides or tetrasulphides), such as, for example, bis(3-trimethoxysilylpropyl) or bis(3-triethoxysilylpropyl)polysulphides. Use is in particular made, among these compounds, of bis(3-triethoxysilylpropyl)tetrasulphide, abbreviated to TESPT, of formula $[(C_2H_5O)_3Si(CH_2)_3S_2]_2$, or bis(3-triethoxysilylpropyl)disulphide, abbreviated to TESPD, of formula $[(C_2HSO)_3 Si(CH_2)_3S]_2$. Mention will also be made, as preferred examples, of bis(mono(C_1-C_4)alkoxyldi(C_1-C_4)alkylsilylpropyl)polysulphides (in particular disulphides, trisulphides or tetrasulphides), more particularly bis(monoethoxydimethylsilylpropyl)tetrasulphide, as described in patent application WO 02/083782 (or US 7 217 751).

[0064] Mention will in particular be made, as coupling agent other than alkoxysilane polysulphide, of bifunctional POSs (polyorganosiloxanes) or of hydroxysilane polysulphides (R^2 = OH in the above formula (I)), such as described in patent applications

WO 02/30939 (or US 6 774 255) and WO 02/31041 (or US 2004/051210), or of silanes or POSs carrying azodicarbonyl functional groups, such as described, for example, in patent applications WO 2006/125532, WO 2006/125533 and WO 2006/125534.

[0065] As examples of other silane sulphides, mention will be made, for example, of the silanes bearing at least one thiol (-SH) function (referred to as mercaptosilanes) and/or at least one blocked thiol function, such as described, for example, in patents or patent applications US 6 849 754, WO 99/09036, WO 2006/023815, WO 2007/098080, WO 2008/055986 and WO 2010/072685.

[0066] Of course, use could also be made of mixtures of the coupling agents described previously, as described in particular in the aforementioned patent application WO 2006/125534.

[0067] According to one preferred embodiment of the invention, the content of coupling agent may be from 0.5 to 15% by weight per 100% by weight of the reinforcing inorganic filler, particularly silica.

[0068] According to one preferred embodiment of the invention, the content of coupling agent may be less than 30 phr (for example, between 0.1 and 30 phr), preferably less than 25 phr (for example, between 0.5 and 25 phr), more preferably less than 20 phr (for example, between 1 and 20 phr), still more preferably less than 15 phr (for example, between 1.5 and 15 phr).

[0069] The rubber composition according to the invention is based on a plasticizing agent.

[0070] The plasticizing agent may comprise a liquid plasticizer(s), a hydrocarbon resin(s), or the mixtures thereof.

[0071] According to one preferred embodiment of the invention, the content of total plasticizing agent is 20 to 100 phr, preferably 25 to 90 phr, more preferably 30 to 80 phr.

[0072] The plasticizing agent in the rubber composition according to the invention comprises more than 4 phr of of a mercapto-modified silicone oil which is one of liquid plasticizer. The indicated minimum or less, the targeted technical effect is insufficient. Preferably, the content of mercapto-modified silicone oil is at least 6 phr, more preferably at least 8 phr, still more preferably at least 10 phr. The mercapto-modified silicone oil is liquid at 20°C (under atmospheric pressure) by definition.

[0073] The mercapto-modified silicone oil means silicone or polymerized siloxanes bearing at least one mercapto (thiol: -SH) function per molecule.

[0074] According to a preferred embodiment of the invention, the weight-average molecular weight (Mw) of mercapto-modified silicone oil may be more than 500 g/mol (for example, between 500 and 50000 g/mol), preferably more than 1000 g/mol (for example, between 1000 and 40000 g/mol), more preferably more than 3000 g/mol (for example, between 3000 and 30000 g/mol), still more preferably at least 5000 g/mol (for example, from 5000 to 20000 g/mol). The weight-average molecular weight of mercapto-modified silicone oil may be determined by gel permeation chromatography (ambient temperature (for example, 20°C), polystyrene standard; μ styragem columns; eluent THF (tetrahydrofuran) ; flow rate 1 mm/minute; 200μl (microliter) of a solution containing 0.5% by weight of silicone in THF are injected, and detection is performed by "differential refractometer" and "ultra-violet and visible absorption spectrophotometer").

[0075] A fifteenth aspect of the invention is the rubber composition according to any one of the first to the fourteenth aspects, wherein the mercapto-modified silicone oil bears at least two mercapto functions per molecule.

[0076] According to a preferred embodiment of the invention, the functional type of the mercapto-modified silicone oil is selected from the group consisting of side chain, end chain and dual-end that is α, ω difunctional type.

[0077] A sixteenth aspect of the invention is the rubber composition according to any one of the first to the fifteenth aspects, wherein the functional type of the mercapto-modified silicone oil is aα,ωdifunctional type.

[0078] The metcapto-modified silicone oil is well known and is available commercially, for example known as KF-2001, KF-2004, and X-22-167B, as provided by Shin-Etsu Chemical Co., Ltd.

[0079] A seventeenth aspect of the invention is the rubber composition according to any one of the first to the sixteenth aspects, wherein the plasticizing agent comprises between 4 and 40 phr of the mercapto modified silicon oil. Wherein the recommended maximum, there is an issue of cost of the mercapto-modified silicone oil and a risk of worsening processability. Preferably, the content of mercapto modified silicon oil is from 6 to 30 phr, more preferably from 8 to 20 phr, still more preferably from 10 to 15 phr.

[0080] An eighteenth aspect of the invention is the rubber composition according to any one of the first to the seventeenth aspects, wherein the plasticizing agent further comprises a compound selected from the group consisting of at least one liquid plasticizer other than the mercapto-modified silicone oil, at least one hydrocarbon resin and the mixtures thereof.

[0081] The role of the liquid plasticizer is to soften the matrix by diluting the elastomer and the reinforcing filler. The liquid plasticizer is liquid at 20°C by definition, their role is to soften the matrix by diluting the elastomer and the reinforcing filler; their Tg_{DSC} is by definition less than -20°C, preferably less than -30°C, less than -40°C.

[0082] Any extending oil, whether of aromatic or non-aromatic nature, any liquid plasticizing agent known for its plasticizing properties with regard to elastomer matrix(es) (for instance, diene elastomer), can be used as the liquid plasticizer. At ambient temperature (20°C) under atmospheric pressure, these plasticizers or these oils, which are more or less viscous, are liquids (that is to say, as a reminder, substances that have the ability to eventually take on the shape of their container), as opposite to plasticizing hydrocarbon resin(s) which are by nature solid at ambient temperature (20°C) under atmospheric pressure.

[0083] A nineteenth aspect of the invention is the rubber composition according to the eighteenth aspect, wherein the liquid plasticizer other than the mercapto modified silicon oil is selected from the group consisting of liquid diene polymer, polyolefinic oils, naphthenic oils, paraffinic oils, Distillate Aromatic Extracts (DAE) oils, Medium Extracted Solvates (MES) oils, Treated Distillate Aromatic Extracts (TDAE) oils, Residual Aromatic Extracts (RAE) oils, Treated Residual Aromatic Extracts (TRAE) oils, Safety Residual Aromatic Extracts (SRAE) oils, mineral oils, vegetable oils, ether plasticizers, ester plasticizers, phosphate plasticizers, sulphonate plasticizers and the mixtures thereof, preferably selected from the group consisting of MES oils, TDAE oils, naphthenic oils, vegetable oils and the mixtures thereof, more preferably selected from the group consisting of MES oils, vegetable oils and the mixtures thereof, still more preferably selected from the group consisting of vegetable oils and the mixtures thereof. The vegetable oil(s) may be made of an oil selected from the group consisting of linseed, safflower, soybean, corn, cottonseed, turnip seed, castor, tung, pine, sunflower, palm, olive, coconut, groundnut and grapeseed oils, and the mixtures thereof, particularly sunflower oil(s), more particularly sunflower oil(s) containing over 60%, still more particularly over 70%, advantageously over 80%, more advantageously over 90%, still advantageously 100%, by weight of oleic acid.

[0084] The hydrocarbon resin(s) are polymer well known by a person skilled in the art, which are essentially based on carbon and hydrogen, and thus miscible by nature in rubber composition(s), for instance, diene elastomer composition(s). They can be aliphatic or aromatic or also of the aliphatic/aromatic type, that is to say based on aliphatic and/or aromatic monomers. They can be natural or synthetic and may or may not be petroleum-based (if such is the case, also known under the name of petroleum resins). They are preferably exclusively hydrocarbon, that is to say, that they comprise only carbon and hydrogen atoms.

[0085] Preferably, the hydrocarbon resins as being “plasticizing” exhibit at least one, more preferably all, of the following characteristics:

- a Tg_{DSC} of above 20°C (for example between 20°C and 100°C), preferably above 30°C (for example between 30°C and 100°C), more preferably above 40°C (for example between 40°C and 100°C);
- a number-average molecular weight (Mn) of between 400 and 2000 g/mol (more preferably between 500 and 1500 g/mol);
- a polydispersity index (PI) of less than 3, more preferably less than 2 (reminder: PI

= Mw/Mn with Mw the weight-average molecular weight).

[0086] The macrostructure (Mw, Mn and PI) of the hydrocarbon resins is determined by steric exclusion chromatography (SEC): solvent tetrahydrofuran; temperature 35°C; concentration 1 g/l; flow rate 1 ml/min; solution filtered through a filter with a porosity of 0.45μm before injection; Moore calibration with polystyrene standards; set of 3 “Waters” columns in series (“Styragel” HR4E, HR1 and HR0.5); detection by differential refractometer (“Waters 2410”) and its associated operating software (“Waters Empower”).

[0087] A twentieth aspect of the invention is the rubber composition according to the eighteenth aspect, wherein the hydrocarbon resin is selected from the group consisting of cyclopentadiene (abbreviated to CPD) homopolymer or copolymer resins, dicyclopentadiene (abbreviated to DCPD) homopolymer or copolymer resins, terpene homopolymer or copolymer resins, C_5 fraction homopolymer or copolymer resins, C_9 fraction homopolymer or copolymer resins, alpha-methyl styrene homopolymer or copolymer resins and the mixtures thereof. Use is more preferably made, among the above copolymer resins, of those selected from the group consisting of (D)CPD/vinylaromatic copolymer resins, (D)CPD/terpene copolymer resins, (D)CPD/C_5 fraction copolymer resins, (D)CPD/C_9 fraction copolymer resins, terpene/vinylaromatic copolymer resins, terpene/phenol copolymer resins, C_5 fraction/vinyl-aromatic copolymer resins, C_9 fraction/vinylaromatic copolymer resins, and the mixtures thereof.

[0088] The term “terpene” combines here, in a known way, the α-pinene, β-pinene and limonene monomers; use is preferably made of a limonene monomer, which compound exists, in a known way, in the form of three possible isomers: L-limonene (laevorotatory enantiomer), D-limonene (dextrorotatory enantiomer) or else dipentene, the racemate of the dextrorotatory and laevorotatory enantiomers. Styrene, α-methylstyrene, ortho-, meta- or para-methylstyrene, vinyltoluene, para-(tert-butyl)styrene, methoxystyrenes, chlorostyrenes, hydroxystyrenes vinylmesitylene, divinylbenzene, vinylnaphthalene, or any vinylaromatic monomer resulting from a C_9 fraction (or more generally from a C_8 to C_{10} fraction) are suitable, for example, as vinylaromatic monomer. Preferably, the vinylaromatic compound is styrene or a vinylaromatic monomer resulting from a C_9 fraction (or more generally from a C_8 to C_{10} fraction). Preferably, the vinylaromatic compound is the minor monomer, expressed as molar fraction, in the copolymer under consideration.

[0089] The preferred resins above are well known to a person skilled in the art and are commercially available, for example:

- polylimonene resins: by DRT under the name “Dercolyte L120” (Mn=625 g/mol; Mw=1010 g/mol; PI=1.6; Tg_{DSC}=72°C) or by Arizona Chemical Company under the

name "Sylvagum TR7125C" (Mn=630 g/mol; Mw=950 g/mol; PI=1.5; Tg_{DSC}=70°C);
- C_5 fraction/vinylaromatic, notably C_5 fraction/styrene or C_5 fraction/C_9 fraction, copolymer resins: by Neville Chemical Company under the names "Super Nevtac 78", "Super Nevtac 85" or "Super Nevtac 99", by Goodyear Chemicals under the name "Wingtack Extra", by Kolon under the names "Hikorez T1095" and "Hikorez T1100", or by Exxon under the names "Escorez 2101" and "ECR 373";
limonene/styrene copolymer resins: by DRT under the name "Dercolyte TS 105" or by Arizona Chemical Company under the names "ZT115LT" and "ZT5100".

[0090] Mention may also be made, as examples of other preferred resins, of phenol-modified α-methylstirene resins. It should be remembered that, in order to characterize these phenol-modified resins, use is made, in a known way, of a number referred to as "hydroxyl number" (measured according to Standard ISO 4326 and expressed in mg KOH/g). α-Methylstirene resins, in particular those modified with phenol, are well known to a person skilled in the art and are available commercially, for example sold by Arizona Chemical Company under the names "Sylvares SA 100" (Mn=660 g/mol; PI=1.5; Tg_{DSC}=53°C); "Sylvares SA 120" (Mn=1030 g/mol; PI=1.9; Tg_{DSC}=64°C); "Sylvares 540" (Mn=620 g/mol; PI=1.3; Tg_{DSC}=36°C; hydroxyl number=56 mg KOH/g); and "Sylvares 600" (Mn=850 g/mol; PI=1.4; Tg_{DSC}=50°C; hydroxyl number=31 mg KOH/g).

[0091] The rubber composition according to the invention may be based on all or portion(s) of the usual additives generally used in the elastomer compositions intended for the manufacture for tires, in particular for tire treads, such as, for example, protection agents, such as antiozone waxes, chemical antiozonants, antioxidants, reinforcing resins, methylene acceptors (for example phenolic novolak resin) or methylene donors (for example HMT or H3M), a crosslinking system based either on sulphur or on donors of sulphur and/or per oxide and/or bismaleimides, vulcanization accelerators, or vulcanization activators.

[0092] These compositions can be also based on coupling activators when a coupling agent is used, agents for covering the reinforcing inorganic filler 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 property of processing in the raw state; these agents are, for example, hydrolysable silanes, such as alkylalkoxysilanes, polyols, polyethers, amines, or hydroxylated or hydrolysable polyorganosiloxanes.

[0093] The rubber composition according to the invention may be manufactured in appropriate mixers using two successive preparation phases well known to a person skilled in the art: a first phase of thermomechanical working or kneading (referred to as "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 (referred to as "productive" phase) at a lower temperature, typically of less than 110°C, for example between 40°C and 100°C, finishing phase during which the crosslinking or vulcanization system is incorporated.

[0094] A process which can be used for the manufacture of such compositions comprises, for example and preferably, the following steps:

- incorporating in the elastomer matrix, for instance, the diene elastomer(s), in a mixer, the reinforcing filler, during a first stage ("non productive" stage) everything being kneaded thermomechanically (for example in one or more steps) until a maximum temperature of between 110°C and 190°C is reached;
- cooling the combined mixture to a temperature of less than 100°C;
- subsequently incorporating, during a second stage (referred to as a "productive" stage), a crosslinking system;
- kneading everything up to a maximum temperature of less than 110°C;
- extruding or calendering the rubber composition thus obtained, in particular in the form of a tire tread;

wherein the plasticizing agent comprising the mercapto-modified silicone oil is incorporated either during the first stage or during the second stage, or both of the first and second stages.

[0095] According to a preferred embodiment of the invention, the first (non-productive) phase is carried out in a single thermomechanical stage during which all the necessary constituents may be introduced into an appropriate mixer, such as a standard internal mixer, followed, in a second step, for example after kneading for 1 to 2 minutes, by the other additives, optional additional filler-covering agents or processing aids, with the exception of the crosslinking system. The total kneading time, in this non-productive phase, is preferably between 1 and 15 min.

[0096] After cooling the mixture thus obtained, the crosslinking system may be then incorporated at low temperature (for example, between 40°C and 100°C), generally in an external mixer, such as an open mill; the combined mixture is then mixed (the second (productive) phase) for a few minutes, for example between 2 and 15 min.

[0097] According to a specific embodiment of the invention, and combined with the above embodiment described here, the plasticizing agent comprising the mercapto-modified silicone oil may be incorporated partially or totally during the second stage in addition to or instead of the first stage. In this connection, the mercapto-modified silicone oil may be incorporated into the mixer alone or in combination with the remaining plasticizer, which may be included in the essential plasticizing agent of the invention (e.g., the compound selected from the group consisting of at least one liquid plasticizer other than the mercapto-modified silicone oil, at least one hydrocarbon resin and the mixture thereof). For example, the mercapto-modified silicone oil may be incorporated totally during the second stage, while the remaining plasticizing agent may be incorporated totally during the first stage, and vice versa. When the mercapto-modified silicone oil and the remaining plasticizing agent are incorporated into the mixer separately, it is preferable that the mercapto-modified silicone oil is incorporated partially or totally during the second stage in addition to or instead of the first stage and the remaining plasticizing agent is incorporated totally during the first stage.

[0098] The crosslinking system is preferably based on sulphur and on a primary vulcanization accelerator, in particular on an accelerator of sulphenamide type. Added to this vulcanization system are various known secondary accelerators or vulcanization activators, such as zinc oxide, stearic acid, guanidine derivatives (in particular diphenylguanidine), and the like, incorporated during the first non-productive phase and/or during the productive phase. The content of sulphur is preferably between 0.5 and 10.0 phr, more preferably between 0.5 and 3.0 phr, and that of the primary accelerator is preferably between 0.5 and 5.0 phr.

[0099] A twenty first aspect of the invention is the rubber composition according to any one of the first to the twentieth aspects, wherein the rubber composition may be based on a crosslinking system comprising no zinc oxide, or comprising less than 2.0 phr, preferably less than 1.5 phr, more preferably less than 1.0 phr, still more preferably less at least 0.5 phr, which means the crosslinking system comprises 0 to less than 2.0 phr, preferably 0 to less than 1.5 phr, more preferably 0 to less than 1.0 phr, still more preferably 0 to 0.5 phr. Particularly, the crosslinking system is devoid of zinc oxide.

[0100] Use may be made, as accelerator (primary or secondary) of any compound capable of acting as accelerator of the vulcanization of elastomer matrix, for instance, diene elastomers, in the presence of sulphur, in particular accelerators of the thiazoles type and their derivatives, accelerators of thiurams types, or zinc dithiocar bamates. These accelerators are more preferably selected from the group consisting of 2-mercaptobenzothiazyl disulphide (abbreviated to “MBTS”), N-cyclohexyl-2-benzothiazole sulphenamide (abbreviated to “CBS”), N,N-dicyclohexyl-2 benzothiazolesulphenamide (“DCBS”), N-ter‘t-butyl-2-ben zothiazolesulphenamide (“TBBS”), N-tert-butyl-2 benzothiazolesulphenimide (“TBSI”), zinc dibenzyldithiocarbamate (“ZBEC”), Tetrabenzylthiuram disulfide (“TBZTD”) and the mixtures thereof.

[0101] The final composition thus obtained is subsequently calendered, for example in the form of a sheet or of a plaque, in particular for laboratory characterization, or else extruded in the form of a rubber profiled element which may be directly used as tire treads in particularly.

[0102] The vulcanization (or curing) is carried out in a known way at a temperature generally of between 110°C and 190°C for a sufficient time which may vary, for example, between 5 and 90 min depending in particular on the curing temperature, the vulcanization system adopted and the vulcanization kinetics of the composition under consideration.

[0103] The rubber compositions according to the invention can constitute all or a portion only of the tread in accordance with the invention, in the case of a tread of composite type formed from several rubber compositions of different formulations.

[0104] A twenty second aspect of the invention is a tire comprising the rubber composition according to any one of the first to the twenty first aspects.

[0105] A twenty third aspect of the invention is a tire in which the rubber composition according to any one of the first to the twenty first aspects is comprised in its tread and/or sidewall, preferably its tread.

[0106] The tires of the invention are particularly intended to equip passenger motor vehicles, including 4×4 (four-wheel drive) vehicles and SUV (Sport Utility Vehicles) vehicles, and industrial vehicles particularly selected from vans and heavy duty vehicles (i.e., bus or heavy road transport vehicles (lorries, tractors, trailers)).

[0107] The invention may also apply to the cases where the rubber compositions described above form only one part of treads of composite or hybrid type, especially those consisting of two radially superposed layers of different formulations (referred to as “cap-base” construction), that are both patterned and intended to come into contact with the road when the tire is rolling, during the service life of the latter. The base part of the formulation described above could then constitute the radially outer layer of the tread intended to come into contact with the ground from the moment when a new tire starts rolling, or on the other hand its radially inner layer intended to come into contact with the ground at a later stage.

[0108] Moreover, the rubber compositions according to the invention may constitute all or a portion only of sidewalls of tires, which may make it possible to decrease rolling resistance performance of the tires.

[0109] The invention relates to the rubber compositions, to the treads described above and the sidewalls above, both in the raw state (i.e., before curing) and in the cured state (i.e., after crosslinking or vulcanization).

[0110] The invention is further illustrated by the following non-limiting examples.

Example

[0111] In the test, nine rubber compositions identified as T-0 to T-4 (a reference and comparative examples) and C-1 to C-4 (examples according to the invention) are compared. They are based on a diene elastomer (non functionalized SBR or functionalized SBR bearing a SiOR function) reinforced with a blend of silica and carbon black, and a plasticizing agent with/without a dimethyl silicone oil , additionally with/

without zinc oxide. The formulations of the nine rubber compositions, with the content of the various products expressed in phr, and their properties after curing are given at Table 1.

[0112] The reinforcing filler, its associated coupling agent, the plasticizing agent, the elastomer matrix and the various other ingredient, with the exception of the vulcanization system, were successively introduced into an internal mixer having an initial vessel temperature of approximately 60°C; the mixer was thus approximately 70% full (% by volume). Thermomechanical working (non-productive phase) was then carried out in one stage, which lasts in total approximately 3 to 4 minutes, until a maximum "dropping" temperature of 165°C was reached. The mixture thus obtained was recovered and cooled and then sulphur and an accelerator of sulphenamide type were incorporated on an external mixer (homofinisher) at 20 to 30°C, everything being mixed (productive phase) for an appropriate time (for example, between 5 and 12 min).

[0113] The compositions thus obtained were subsequently calendered, either in the form of sheets (thickness of 2 to 3 mm) or of fine sheets of rubber, for the measurement of their physical or mechanical properties, or in the form of profiled elements which could be used directly, after cutting and/or assembling to the desired dimensions, for example as tire semi-finished products, in particular as tire treads.

[0114] The dynamic properties G* and $\tan(\delta)_{max}$ at 23°C were measured on a viscosity analyser (Metravib VA4000), according to the standard ASTM D 5992-96. A recording was made of the response of a sample of vulcanized composition (cylindrical test specimen with a thickness of 4 mm and a cross section of 400 mm^2), subjected to a simple alternating sinusoidal shear stress, at the frequency of 10Hz, under defined temperature conditions, for example at 23°C according to the standard ASTM D 1349-99, or depending on the case at a different temperature. A strain amplitude sweep was carried out from 0.1% to 100% (outward cycle), then from 100% to 1% (return cycle). The results utilized were the complex dynamic shear modulus G* and the loss factor tan(δ). For the return cycle, the maximum value of tan(δ) observed, identified as $\tan(\delta)_{max}$, and also the complex dynamic shear modulus G* at 10% strain, at 23°C, were indicated.

[0115] It is generally said by a person skilled in the art that the value of complex dynamic shear modulus G* at 10% strain, at 23°C, is representative of low strain stiffness of the material, and the greater low strain stiffness of the rubber composition is, the better the road behavior of the tire comprising the rubber composition is. Values are expressed as road behavior performance, therefore a value greater than that of the reference composition T-1, set at 100, indicates an improved performance.

[0116] It is recalled that, in a manner well known to a person skilled in the art, the value of $\tan(\delta)_{max}$ at 23°C is representative of the hysteresis of the material, and therefore of the rolling resistance: the lower tan(δ)$_{max}$ at 23°C of the rubber composition is, the lower the rolling resistance of the tire comprising the rubber composition is. Values are expressed as rolling resistance performance therefore a value greater than that of the reference composition T-1, set at 100, indicates an improved performance.

[0117] The results from Table 1 demonstrate that the rubber compositions (C-1 to C-4) according to the invention have an unexpectedly improved balance of performances between low strain stiffness and hysteresis than that of the reference or comparative examples (T-0 to T-4).

[0118] In conclusion, the rubber composition according to the invention allows an improvement of the balance of performances between road behavior and rolling resistance of the tire as represented by low strain stiffness and hysteresis.

[0119] [Table 1]

Rubber composition(s)	T-0	T-1	T-2	C-1	C-2	T-3	C-3	T-4	C-4
BR (1)	20	20	20	20	20	20	20	80	80
SBR1 (2)	80	80							
SBR2 (3)			80	80	80				
SBR3 (4)						80	80	20	20
Carbon black (5)	3	3	3	3	3	3	3	3	3
Silica (6)	110	110	110	110	110	110	110	110	110
Coupling agent (7)	8.8	8.8	8.8	8.8	8.8	8.8	8.8	8.8	8.8
Hydrocarbon resin (8)	60	55	60	55	55	60	55	60	55
Liquid plasticizer (9)	15	10	15	10	10	15	10	15	10
Mercapto-modified silicone oil (10)		10		10	10		10		10
ZnO	0.9	0.9	0.9	0.9		0.9	0.9	0.9	0.9
Stearic acid	2	2	2	2	2	2	2	2	2
Antiozone wax	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9
Antioxidant (11)	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
DPG (12)	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
Sulphur	1	1	1	1	1	1	1	1	1
Accelerator (13)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Properties after vulcanization									
G*(10%, 23℃, 10Hz)	96	100	66	69	67	90	86	95	97
Tan(δ)$_{max}$ [10%, 23℃, 10Hz]	89	100	122	139	144	108	122	105	111
Balance of performances between low strain stiffness and hysteresis	92	100	94	104	106	99	104	100	104

(1) BR: BR with 0.3% of 1,2 vinyl; 2.7% of trans; 97% of cis-1,4 (Tg_{DSC} = -105°C);

(2) SBR1: non functionalized solution SBR with 27% of styrene unit and 24% of unit 1,2 of the butadiene part (Tg_{DSC} = -48°C);

(3) SBR2: functionalized solution SBR with 27% of styrene unit and 24 % of unit 1,2

of the butadiene part (Tg_{DSC} = -48°C) bearing a SiOR function, R being a methyl radical, the SiOR function not located at the ends of the elastomer chain; wherein the silicon atom of the SiOR function is inserted between the carbon-carbon bonds of the elastomer chain; the SBR further bearing a tertiary amine function made of the amine substituted with two methyl radicals; wherein the nitrogen atom of the amine function is not inserted between the carbon-carbon of the elastomer chain, and the SiOR function bears the amine function; the SBR prepared according to a process described in a patent EP 2 285 852 B1;

(4) SBR3: functionalized solution SBR with 27% of styrene unit and 24% of unit 1,2 of the butadiene part (Tg_{DSC} = -48°C) bearing a SiOR function, R being a hydrogen atom, the SiOR being dimethylsilanol function at the end of the elastomer chain, the SBR prepared according to a process described in a patent EP 0 778 311 B1;

(5) Carbon black: Carbon black (ASTM grade N234 from Cabot);

(6) Silica: Silica ("Zeosil 1165MP" from Rhodia (CTAB, BET: about 160 m^2/g));

(7) Coupling agent TESPT ("Si69" from Evonik);

(8) Cycloaliphatic hydrocarbon resins ("ESCOREZ5600" from ExxonMobil, Tg_{DSC} =52°C);

(9) Oleic sunflower oil ("Agripure 80" from Cargill, Weight percent oleic acid: 100%);

(10) α, ω difunctional (Dual-end) type mercapto-modified silicone fluids ("X-22-167B" (Mw: 10000) from Shin-Etsu Chemical Co., Ltd.);

(11) N-(1,3-dimethylbutyl)-N-phenyl-para-phenylenediamine ("Santoflex 6-PPD" from Flexsys);

(12) Diphenylguanidine ("Perkacit DPG" from Flexsys);

(13) N-dicyclohexyl-2-benzothiazolesulphenamide ("Santocure CBS" from Flexsys);

Claims

[Claim 1] A rubber composition based on at least:
- an elastomer matrix comprising 10 to 100 phr of a first diene elastomer bearing at least one SiOR function, R being a hydrogen atom or a hydrocarbon radical, and optionally, 0 to 90 phr of a second diene elastomer which is different from the first diene elastomer;
- a reinforcing filler comprising at least 60 phr of a reinforcing inorganic filler; and
- a plasticizing agent comprising more than 4 phr of a mercapto-modified silicone oil.

[Claim 2] The rubber composition according to Claim 1, wherein the first diene elastomer is a styrene-butadiene copolymer.

[Claim 3] The rubber composition according to Claim 1 or Claim 2, wherein the SiOR function is located at the chain end of the first diene elastomer.

[Claim 4] The rubber composition according to Claim 1 or Claim 2, wherein the SiOR function is not located at the chain ends of the first diene elastomer.

[Claim 5] The rubber composition according to any one of Claims 1 to 4, wherein the first diene elastomer further bears at least one amine function.

[Claim 6] The rubber composition according to Claim 5, wherein the SiOR function bears the amine function.

[Claim 7] The rubber composition according to any one of Claims 1 to 6, wherein R of the SiOR function is a hydrogen atom.

[Claim 8] The rubber composition according to any one of Claims 1 to 6, wherein R of the SiOR function is a hydrocarbon radical.

[Claim 9] The rubber composition according to any one of Claims 1 to 8, wherein the first diene elastomer has a glass transition temperature of lower than -40°C.

[Claim 10] The rubber composition according to any one of Claims 1 to 9, wherein the second diene elastomer is selected from the group consisting of polybutadienes, natural rubber, synthetic polyisoprenes, butadiene copolymers, isoprene copolymers and the mixtures thereof.

[Claim 11] The rubber composition according to Claim 10, wherein the second diene elastomer is a polybutadiene.

[Claim 12] The rubber composition according to any one of Claims 1 to 11, wherein the reinforcing filler comprises 60 to 200 phr of the reinforcing inorganic filler.

[Claim 13] The rubber composition according to any one of Claims 1 to 12, wherein the reinforcing inorganic filler predominately comprises silica.

[Claim 14] The rubber composition according to any one of Claims 1 to 13, wherein the reinforcing filler comprises less than 40 phr of carbon black.

[Claim 15] The rubber composition according to any one of Claims 1 to 14, wherein the mercapto-modified silicone oil bears at least two mercapto functions per molecule.

[Claim 16] The rubber composition according to any one of Claims 1 to 15, wherein the functional type of the mercapto-modified silicone oil is aα,ωdifunctional type.

[Claim 17] The rubber composition according to any one of Claims 1 to 16, wherein the plasticizing agent comprises between 4 and 40 phr of the mercapto modified silicon oil.

[Claim 18] The rubber composition according to any one of Claims 1 to 17, wherein the plasticizing agent further comprises a compound selected from the group consisting of at least one liquid plasticizer other than the mercapto-modified silicone oil, at least one hydrocarbon resin and the mixtures thereof.

[Claim 19] The rubber composition according to Claim 18, wherein the liquid plasticizer other than the mercapto-modified silicone oil is selected from the group consisting of liquid diene polymers, polyolefinic oils, naphthenic oils, paraffinic oils, Distillate Aromatic Extracts (DAE) oils, Medium Extracted Solvates (MES) oils, Treated Distillate Aromatic Extracts (TDAE) oils, Residual Aromatic Extracts (RAE) oils, Treated Residual Aromatic Extracts (TRAE) oils, Safety Residual Aromatic Extracts (SRAE) oils, mineral oils, vegetable oils, ether plasticizers, ester plasticizers, phosphate plasticizers, sulphonate plasticizers and the mixtures thereof.

[Claim 20] The rubber composition according to Claim 18, wherein the hydrocarbon resin is selected from the group consisting of cyclopentadiene homopolymer or copolymer resins, dicyclopentadiene homopolymer or copolymer resins, terpene homopolymer or copolymer resins, C_5 fraction homopolymer or copolymer resins, C_9 fraction homopolymer or copolymer resins, alpha-methyl styrene homopolymer or copolymer resins, and the mixtures thereof.

[Claim 21] The rubber composition according to any one of Claims 1 to 20, wherein the rubber composition is based on a crosslinking system comprising no zinc oxide, or comprising less than 2.0 phr.

[Claim 22] A tire comprising the rubber composition according to any one of Claims 1 to 21.

[Claim 23] A tire according to Claim 22 in which the rubber composition according to any one of Claims 1 to 21 is comprised in its tread and / or its sidewall.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/026083

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C08L15/00(2006.01)i, B60C1/00(2006.01)i, C08K3/00(2006.01)i, C08L9/00(2006.01)i, C08L83/06(2006.01)i

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)

Int.Cl. C08L1/00-101/14, B60C1/00-19/12, C08K3/00-13/08, C08C19/00-19/44, C08F6/00-246/00,301/00

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2017
Registered utility model specifications of Japan 1996-2017
Published registered utility model applications of Japan 1994-2017

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 2016/0009846 A1 (THE YOKOHAMA RUBBER CO.,	1-23

☑ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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

Date of the actual completion of the international search
06.10.2017

Date of mailing of the international search report
24.10.2017

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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