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(54) Title: AN ARTICLE, IN PARTICULAR A TIRE

(57) Abstract: An article comprises a portion comprising a contact element having a height (H) (mm), a contact surface intended to come into contact with the ground, and an area (S) (mm²) of the contact surface, the contact element comprising a rubber composition based on at least an elastomer matrix, a reinforcing filler, a plasticizing agent, and more than 10 phr of reinforcing fibers extending substantially perpendicularly to the surface of the ground; wherein a ratio by weight of the plasticizing agent to the reinforcing filler is more than 1.0.



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Description

Title of Invention: AN ARTICLE, IN PARTICULAR A TIRE

Technical Field

[0001] The field of the invention is that of articles, for example, tires, shoes, conveyors or caterpillar tracks, in particular for tire treads, and that of production methods of the articles.

Background Art

[0002] It is known that functions of an article, especially a tire, intended to bring an object and to come into contact with the ground are mainly to support the load of the object, to transmit forces to the ground surface, to absorb shocks from the ground, and to change and maintain the direction of travel.

[0003] The first and the third functions are inconsistent with each other, so that a constant objective of manufacturers for articles (for example, tires) is to improve the balance of these functions.

Summary of Invention

Technical Problem

[0004] During the research, the inventor has discovered that a specific contact element of a portion intended in particular for a rubber article, in particular, a tire, a shoe, a conveyor or a caterpillar track, in more particular for a tire, which allows unexpectedly improved the balance of the above functions.

[0005] In the present description, unless expressly stated otherwise, all the percentages (%) indicated are percentages by weight (wt%).

[0006] The expression “elastomer matrix” is understood to mean, in a given composition, all of the elastomers present in said rubber composition.

[0007] The abbreviation “phr” signifies parts by weight per hundred parts by weight of the elastomer matrix in the considered rubber composition.

[0008] In the present description, unless expressly indicated otherwise, each T_{gDSC} (glass transition temperature) is measured in a known way by DSC (Differential Scanning Calorimetry) according to Standard ASTM D3418-08.

[0009] Any interval of values denoted by the expression “between a and b” represents the range of values of more 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).

[0010] The expression “based on” should be understood in the present application to mean a composition comprising the mixture(s), the product of the reaction of the various constituents used or both, 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).

[0011] As a tire has a geometry of revolution about an axis of rotation, the geometry of the tire is generally described in a meridian plane containing the axis of rotation of the tire, and the following definitions of directions of the tire are understood in the present application:

- A radial direction is a direction perpendicular to the axis of rotation of the tire;
- An axial direction is a direction parallel to the axis of rotation of the tire;
- A circumferential direction is a direction perpendicular to the meridian plane.

[0012] A plane being perpendicular to the axis of rotation of the tire and passing through the middle of a tread surface of the tire is referred to as an equatorial plane of the tire.

[0013] In what follows, expressions “radially”, “axially” and “circumferentially” respectively mean “in the radial direction”, “in the axial direction” and “in the circumferential direction”. Expressions “radially on the inside (radially inner or radially internal), or respectively radially on the outside (radially outer or radially external)” mean “closer or, respectively, further away, from the axis of rotation of the tire, in the radial direction, than”. Expressions “axially on the inside (axially inner or axially interior) or respectively axially on the outside (axially outer or axially exterior)” mean “closer or, respectively further away, from the equatorial plane, in the axial direction, than”. Respective dimensions of a given element in the radial, axial and circumferential directions will also be denoted “radial thickness or height”, “axial width” and “circumferential length” of this element. Expression “laterally” means “in the circumferential or axial direction”.

[0014] The expression “X extending substantially perpendicularly to Y” (or the expression “X substantially perpendicular to Y”) may mean the angle from the extending direction of X to Y is from 80 to 100 degrees, preferably from 85 to 95 degree.

[0015] The expression “X extending substantially parallelly to Y” (or the expression “X substantially parallel to Y”) may mean the angle from the extending direction of X to Y is from -10 to 10 degrees, preferably from -5 to 5 degree.

Solution to Problem

[0016] A first aspect of the invention is an article comprising a portion comprising a contact element having a height (H) (mm) and a contact surface area (S) (mm²) intended to come into contact with the ground, the contact element comprising a rubber composition based on at least an elastomer matrix, a reinforcing filler, a plasticizing agent, and more than 10 phr (for example, between 15 and 90 phr) of reinforcing fibers extending substantially perpendicularly to the surface of the ground;

wherein a ratio by weight of the plasticizing agent to the reinforcing filler is more

than 1.0 (for example, between 1.0 and 10.0).

[0017] According to a preferred embodiment of the first aspect, the contact element is a plate, the height (H) is equal to a distance from the contact surface to the furthest point of the plate in a direction perpendicular to the contact surface of the plate.

[0018] According to another preferred embodiment of the first aspect, the contact element(s) consists of a plurality of pieces (ribs, blocks or the combination thereof) delimited by at least one groove with which the portion is provided, the height (H) is equal to average of distance(s) from the contact surface to the bottom(s) of the groove(s) in a direction perpendicular to the contact surface of the plate.

Advantageous Effects of Invention

[0019] The specific contact element allows unexpectedly improved the balance of the load supporting function and the shock absorption function of the article.

[0020] Each of the below aspect(s), the embodiment(s) and the variant(s) including each of the preferred range(s), matter(s) or combinations thereof 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.

[0021] The rubber composition of the contact element of the portion of the article according to the invention is based on an elastomer matrix.

[0022] 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).

[0023] 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%.

[0024] Although it applies to any type of diene elastomer, a person skilled in the art of rubbers will understand that the invention is preferably employed with essentially unsaturated diene elastomers.

[0025] 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.

[0026] The following are suitable in particular as conjugated dienes: 1,3-butadiene, 2-methyl-1,3-butadiene, 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. 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.

[0027] A second aspect of the invention is the article according to the first aspect, wherein the elastomer matrix comprises at least one diene elastomer selected from the group consisting of natural rubber (NR), synthetic polyisoprenes (IRs), polybutadienes (BRs), butadiene copolymers, isoprene copolymers and combinations thereof; such copolymers are preferably selected from the group consisting of butadiene copolymers and combinations thereof, more preferably selected from the group consisting of styrene-butadiene copolymers (SBR), butadiene-isoprene copolymers (BIR), styrene-isoprene copolymers (SIR), styrene-butadiene-isoprene copolymers (SBIR) and combinations thereof, still more preferably selected from the group consisting of styrene-butadiene copolymers (SBR) and combinations thereof.

[0028] The diene elastomer may have any microstructure which depends on the polymerization conditions used, in particular on the presence or absence of a modifying agent, randomizing agent or both agents, and on the amounts of modifying agent, randomizing agent or both employed. This elastomer may, for example, be a block, statistical, sequential or micro sequential elastomer and may be prepared in dispersion or in solution. This elastomer may be coupled, star-branched or both; or else functionalized with a coupling, star-branching or both; or functionalizing agent.

[0029] A third aspect of the invention is the article according to the first aspect or the second aspect, wherein the elastomer matrix comprises more than 50 phr (for example, more than 50 phr and up to 100 phr), preferably more than 60 phr (for example, between 60 and 90 phr), of a first diene elastomer which is a styrene-butadiene copolymer, advantageously a solution styrene-butadiene copolymer, and optionally comprising less than 50 phr (for example, 0 phr to less than 50 phr), preferably less than 40 phr (for example, between 10 and 40 phr), of a second diene elastomer which is different from

the first diene elastomer, preferably polybutadiene, more preferably having a content (molar %) of 1,2-units of between 4% and 80% or having a content (molar %) of cis-1,4-units of more than 80%, still more preferably more than 90% (molar %), particularly more than or equal to 96% (molar %).

- [0030] According to a preferred embodiment of the second aspect or the third aspect, the styrene-butadiene copolymer may exhibit a styrene unit of less than 30% by weight (for example, between 3 and 30% by weight) per 100% by weight of the styrene-butadiene copolymer, preferably less than 27% by weight (for example, between 5 and 27% by weight), more preferably less than 23% by weight (for example, between 7 and 23% by weight), still more preferably less than 20% by weight (for example, between 10 and 20% by weight), particularly at most 18% by weight (for example, from 12 to 18%). The styrene unit can be determined by ¹H NMR method in accordance with ISO 21561.
- [0031] According to a more preferred embodiment of the second aspect, the third aspect or the preferred embodiment, the styrene-butadiene copolymer may exhibit a glass transition temperature of less than -40°C (for example, between -40°C and -110°C), preferably less than -45°C (for example, between -45°C and -105°C).
- [0032] The rubber composition of the contact element of the portion of the article according to the invention is based on a reinforcing filler.
- [0033] A fourth aspect of the invention is the article according to any one of the first to the third aspects, wherein the reinforcing filler comprises less than 65 phr (for example, between 5 and 65 phr), preferably less than 60 phr (for example, between 10 and 60 phr), less preferably 55 phr (for example, between 15 and 55 phr), still more preferably less than 50 phr (for example, between 20 and 50 phr), particularly less than 45 phr (for example, between 25 and 45 phr), of a reinforcing filler.
- [0034] The reinforcing filler may comprise a reinforcing inorganic filler (for example, silica), carbon black or combinations thereof.
- [0035] A fifth aspect of the invention is the article according to any one of the first to the fourth aspects, wherein the reinforcing filler predominately comprises a reinforcing inorganic filler, that means, the reinforcing filler comprises more than 50% by weight of the reinforcing inorganic filler per 100% of the reinforcing filler. Preferably, the content of the reinforcing inorganic filler is more than 60% by weight, more preferably more than 70% by weight, still more preferably more than 80% by weight, particularly more than 90% by weight, per 100% of the reinforcing filler.
- [0036] 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 in-

intermediate coupling agent, a rubber composition intended for the manufacture, especially the tire manufactures, in other words capable of replacing, in its reinforcing role, a conventional grade, especially tire-grade, carbon black; such a filler is generally characterized, in a known manner, by the presence of hydroxyl (-OH) groups at its surface.

[0037] 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, aluminous or both fillers is described hereafter.

[0038] Mineral fillers of the siliceous type, preferably silica (SiO_2), the aluminous type, preferably alumina (Al_2O_3) or combinations thereof are suitable in particular as the reinforcing inorganic fillers.

[0039] A sixth aspect of the invention is the article according to the fifth 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 reinforcing inorganic filler may comprise 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.

[0040] 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 .

[0041] 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

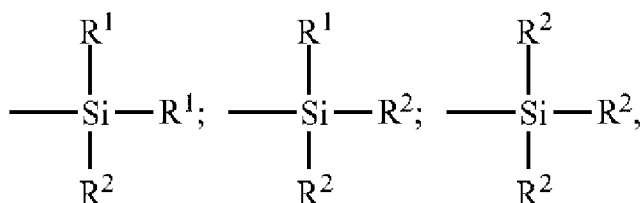
American Chemical Society”, Vol. 60, page 309, February 1938, and more specifically, in accordance with the French standard NF ISO 9277 of December 1996 (multipoint volumetric method (5 points); where gas: nitrogen, degassing: 1 hour at 160°C, relative pressure range p/po: 0.05 to 0.17). The CTAB specific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

- [0042] 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.
- [0043] A seventh aspect of the invention is the article according to any one of the first to the sixth aspects, wherein the reinforcing filler comprises less than 20 phr (for example, between 0 and 20 phr), preferably less than 15 phr (for example, between 0.5 and 15 phr), more preferably less than 10 phr (for example, between 1.0 and 10 phr), still more preferably less than 7.5 phr (for example, between 1.5 and 7.5 phr), particularly less than 5.0 phr (for example, between 2.0 and 5.0 phr), of carbon black.
- [0044] 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 high grip on normal road (especially on wet ground), and snowy ground.
- [0045] 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, physical nature or both, 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.
- [0046] Use can be made in particular of silane polysulfides, 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.
- [0047] Particularly suitable silane polysulfides correspond to the following general formula (I):
- (I) $Z - A - S_x - A - Z$, in which:
- x is an integer from 2 to 8 (preferably from 2 to 5);

- A is a divalent hydrocarbon radical (preferably, C₁-C₁₈ alkylene groups or C₆-C₁₂ arylene groups, more particularly C₁-C₁₀, in particular C₁-C₄, alkenes, especially propylene);

- Z corresponds to one of the formulae below:

[Chem.1]



in which:

- the R¹ radicals which are unsubstituted or substituted and identical to or different from one another, represent a C₁-C₁₈ alkyl, C₅-C₁₈ cycloalkyl or C₆-C₁₈ aryl group (preferably, C₁-C₆ alkyl, cyclohexyl or phenyl groups, in particular C₁-C₄ alkyl groups, more particularly methyl, ethyl or both),

- the R² radicals which are unsubstituted or substituted and identical to or different from one another, represent a C₁-C₁₈ alkoxy or C₅-C₁₈ cycloalkoxy group (preferably a group selected from C₁-C₈ alkoxy and C₅-C₈ cycloalkoxy, more preferably a group selected from C₁-C₄ alkoxy, in particular methoxy and ethoxy), are suitable in particular, without limitation of the above definition.

[0048] In the case of a mixture of alkoxy silane polysulfides 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 alkoxy silane disulfides (x = 2).

[0049] Mention will more particularly be made, as examples of silane polysulfides, of bis((C₁-C₄)alkoxy(C₁-C₄)alkylsilyl(C₁-C₄)alkyl)polysulfides (in particular disulfides, trisulfides or tetrasulfides), such as, for example, bis(3-trimethoxysilylpropyl) or bis(3-triethoxysilylpropyl)polysulfides. Use is in particular made, among these compounds, of bis(3-triethoxysilylpropyl)tetrasulfide, abbreviated to TESPT, of formula [(C₂H₅O)₃Si(CH₂)₃S₂]₂, or bis(3-triethoxysilylpropyl)disulfide, abbreviated to TESP, of formula [(C₂H₅O)₃Si(CH₂)₃S]₂. Mention will also be made, as preferred examples, of bis(mono(C₁-C₄)alkoxydi(C₁-C₄)alkylsilylpropyl)polysulfides (in particular disulfides, trisulfides or tetrasulfides), more particularly bis(monoethoxydimethylsilylpropyl)tetrasulfide, as described in patent application WO 02/083782 (or US 7 217 751).

[0050] Mention will in particular be made, as coupling agent other than alkoxy silane polysulfide, of bifunctional POSs (polyorganosiloxanes) or of hydroxy silane poly-

sulfides ($R^2 = OH$ 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.

- [0051] As examples of other silane sulfides, mention will be made, for example, of the silanes bearing at least one thiol (-SH) function (referred to as mercaptosilanes), at least one blocked thiol function or both, 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.
- [0052] 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.
- [0053] According to a 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.
- [0054] According to a preferred embodiment of the invention, the rubber composition may be based on less than 10 phr (for example, between 0 and 10 phr), preferably less than 8 phr (for example, between 0.1 and 8 phr), more preferably less than 6 phr (for example, between 0.5 and 6 phr), still more preferably less than 4 phr (for example, between 1 and 4 phr), of coupling agent.
- [0055] The rubber composition of the contact element of the portion of the article according to the invention is based on a plasticizing agent.
- [0056] The role of the plasticizing agent is to soften the matrix by diluting the elastomer and the reinforcing filler, and also to reduce shear force to the composition during mixing, which can prevent the mechanical action during the mixing from chopping the reinforcing fibers.
- [0057] An eighth aspect of the invention is the article according to any one of the first to the seventh aspects, wherein amount of plasticizing agent is more than 70 phr (for example, between 70 and 130 phr), preferably more than 75 phr (for example, between 75 and 125 phr), more preferably more than 80 phr (for example, between 80 and 120 phr), still more preferably more than 85 phr (for example, between 85 and 115 phr), particularly more than 90 phr (for example, between 90 and 110 phr), more particularly at least 95 phr (for example, from 95 to 105 phr).
- [0058] A ninth aspect of the invention is the article according to any one of the first to the eighth aspects, wherein the ratio by weight of the plasticizing agent to the reinforcing filler is more than 1.5 (for example, between 1.5 and 7.5), preferably more than 2.0 (for example, between 2.0 and 5.0), more preferably more than 2.5 (for example,

between 2.5 and 3.5).

- [0059] A tenth aspect of the invention is the article according to any one of the first to the ninth aspects, wherein the plasticizing agent is selected from the group consisting of liquid plasticizer(s), hydrocarbon resin(s) and combinations thereof.
- [0060] 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 elastomers, can be used as the liquid plasticizer(s) to soften the matrix by diluting the elastomer and the reinforcing filler. 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.
- [0061] According to a preferred embodiment of the tenth aspect, the plasticizing agent comprises the liquid plasticizer(s) 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 (TRAЕ) oils, Safety Residual Aromatic Extracts (SRAE) oils, mineral oils, vegetable oils, ether plasticizers, ester plasticizers, phosphate plasticizers, sulfonate plasticizers and combinations thereof, preferably selected from the group consisting of MES oils, TDAE oils, naphthenic oils, vegetable oils and combinations thereof, more preferably selected from the group consisting of MES oils, vegetable oils and combinations thereof, still more preferably selected from the group consisting of vegetable oils and combinations 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 combinations thereof, particularly sunflower oil(s), more particularly sunflower oil(s) containing more than 60%, still more particularly more than 70%, advantageously more than 80%, more advantageously more than 90%, still more advantageously 100%, by weight of oleic acid.
- [0062] According to a preferred embodiment of the tenth aspect, the plasticizing agent comprises no liquid plasticizer or comprises less than 50 phr, preferably between 0 and 45 phr, more preferably between 0 and 40 phr, still more preferably between 0 and 35 phr, particularly between 0 and 30 phr, more particularly between 5 and 30 phr, still more particularly between 10 and 30 phr, of the liquid plasticizer(s).
- [0063] 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, aromatic or both 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.

[0064] Preferably, the hydrocarbon resins as being “plasticizing” exhibit at least one, more preferably all, of the following characteristics:

- a T_{gDSC} of more than 20°C (for example, between 20°C and 100°C), preferably more than 30°C (for example, between 30°C and 100°C), more preferably more than 40°C (for example, between 40°C and 100°C);
- a number-average molecular weight (M_n) 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: $PI = M_w/M_n$ with M_w the weight-average molecular weight).

[0065] The macrostructure (M_w , M_n 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 0.45 μm 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”).

[0066] According to a preferred embodiment of the tenth aspect, the plasticizing agent comprises the hydrocarbon resin(s) 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 combinations 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 combinations thereof.

[0067] 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 C₉ fraction (or more generally from a C₈ to C₁₀ fraction) are suitable, for example, as vinylaromatic monomer. Preferably, the vinylaromatic compound is styrene or a vinylaromatic monomer resulting from a C₉ fraction (or more generally from a C₈ to C₁₀ fraction). Preferably, the vinylaromatic compound is the minor monomer, expressed as molar fraction, in the copolymer under consideration.

[0068] 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);
- C₅ fraction/vylaromatic, notably C₅ fraction/styrene or C₅ fraction/C₉ fraction, copolymer resins: by Neville Chemical Company under the names “Super Nevtag 78”, “Super Nevtag 85” or “Super Nevtag 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”.

[0069] Mention may also be made, as examples of other preferred resins, of phenol-modified α -methylstyrene 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 -Methylstyrene 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).

[0070] According to a preferred embodiment of the tenth aspect, the plasticizing agent comprises between 20 and 130 phr, preferably between 25 and 125 phr, more preferably between 30 and 120 phr, still more preferably between 35 and 115 phr, particularly between 40 and 110 phr, more particularly between 45 and 105 phr, still more particularly between 50 and 100 phr, of the hydrocarbon resin(s).

- [0071] An eleventh aspect of the invention is the article according to the tenth aspect, wherein a ratio by weight of the hydrocarbon resin(s) to the liquid plasticizer(s) is more than 0.5, preferably more than 1.0, more preferably more than 1.5, still more preferably more than 2.0, particularly more than 2.5, more particularly more than 3.0, still more particularly more than 3.5.
- [0072] The rubber composition of the contact element of the portion of the article according to the invention is based on more than 10 phr of reinforcing fibers extending substantially perpendicularly to the surface of the ground.
- [0073] The reinforcing fibers may be reinforcing organic fibers, reinforcing inorganic fibers or the combination thereof. The reinforcing organic fibers are fibers made of organic compound(s). The reinforcing inorganic fibers are fibers made of inorganic compound(s).
- [0074] A twelfth aspect of the invention is the article according to any one of the first to the eleventh aspects, wherein the amount of reinforcing fibers is more than 15 phr (for example, between 15 and 85 phr), preferably more than 20 phr (for example, between 20 and 80 phr), more preferably more than 25 phr (for example, between 25 and 75 phr), still more preferably at least 30 phr (for example, from 30 to 70 phr), particularly at least 35 phr (for example, from 45 to 65 phr), more particularly at least 40 phr (for example, from 40 to 60 phr), still more particularly at least 45 phr (for example, from 45 to 55 phr).
- [0075] A thirteenth aspect of the invention is the article according to any one of the first to the twelfth aspects, wherein the volume average length of reinforcing fibers is at least 1.0 mm (for example, from 1.0 to 15.0 mm), preferably at least 1.5 mm (for example, from 1.5 to 14.0 mm), more preferably at least 2.0 mm (for example, from 2.0 to 13.0 mm), still more preferably at least 2.5 mm (for example, from 2.5 to 12.0 mm), particularly at least 3.0 mm (for example, from 3.0 to 11.0 mm), more particularly at least 3.5 mm (for example, from 3.5 to 10.0 mm), before incorporating the reinforcing fibers into the rubber composition.
- [0076] The volume average length of reinforcing fibers (L_v) is defined that corresponds to:

$$L_v = \{\sum(L_i \times V_i)\} / (\sum V_i)$$

$$= [\sum \{L_i \times \pi \times (D/2)^2 \times L_i \times n_i\}] / [\sum \{\pi \times (D/2)^2 \times L_i \times n_i\}]$$

$$= \{\sum(L_i^2 \times n_i)\} / \{\sum(L_i \times n_i)\}$$
 wherein L_i is the length of the i^{th} reinforcing fiber(s), n_i is the number of reinforcing fiber(s) having the length of L_i , V_i is the volume of reinforcing fiber(s) having the length of L_i , and D is the diameter of reinforcing fibers. The above formula assumes that the diameter of reinforcing fibers is constant.
- [0077] According to a preferred embodiment of the invention, the diameter of reinforcing fibers is between 1 and 50 μm , preferably between 3 and 20 μm , more preferably

between 5 and 15 μm before incorporating the reinforcing fibers into the rubber composition.

[0078] The length (and the diameter if necessary) of each reinforcing fiber before incorporating the reinforcing fibers into the rubber composition may be determined in accordance with a method described below and used for the present examples, that is, by observing the reinforcing fibers with an optical microscope.

[0079] A fourteenth aspect of the invention is the article according to any one of the first to the thirteenth aspects, wherein the volume average length of reinforcing fibers is more than 0.5 mm (for example, between 0.5 and 15.0 mm), preferably more than 1.0 mm (for example, between 1.0 and 14.0 mm), more preferably more than 1.5 mm (for example, between 1.5 and 13.0 mm), still more preferably more than 2.0 mm (for example, between 2.0 and 12.0 mm), particularly more than 2.5 mm (for example, between 2.5 and 11.0 mm), more particularly more than 3.0 mm (for example, between 3.0 and 10.0 mm), in the mixed state.

[0080] According to a preferred embodiment of the invention, the diameter of reinforcing fibers is between 1 and 50 μm , preferably between 3 and 20 μm , more preferably between 5 and 15 μm , in the mixed state.

[0081] The mixed state is a state after incorporating the reinforcing fiber into the rubber composition of the contact element of the portion of the article according to the invention.

[0082] A fifteenth aspect of the invention is the article according to any one of the first to the fourteenth aspects, wherein the volume average length of reinforcing fibers is more than 0.5 mm (for example, between 0.5 and 15.0 mm), preferably more than 1.0 mm (for example, between 1.0 and 14.0 mm), more preferably more than 1.5 mm (for example, between 1.5 and 13.0 mm), still more preferably more than 2.0 mm (for example, between 2.0 and 12.0 mm), particularly more than 2.5 mm (for example, between 2.5 and 11.0 mm), more particularly more than 3.0 mm (for example, between 3.0 and 10.0 mm), in the cured state.

[0083] According to a preferred embodiment of the invention, the diameter of reinforcing fibers is between 1 and 50 μm , preferably between 3 and 20 μm , more preferably between 5 and 15 μm , in the cured state.

[0084] The cured state is a state after curing the rubber composition of the contact element of the portion of the article according to the invention.

[0085] The length (and the diameter if necessary) of each reinforcing fiber may be determined by observing the rubber composition in the mixed state, especially in the cured state, with a three dimensional measurement X-ray analyzer, preferably determined in accordance with a method described below and used for the present examples.

- [0086] A sixteenth aspect of the invention is the article according to any one of the first to the fifteenth aspects, wherein the reinforcing fibers are covered with glue, preferably resorcinol formaldehyde latex (RFL) glue. Such glue can enhance adhesiveness of the reinforcing fibers to the elastomer matrix.
- [0087] A seventeenth aspect of the invention is the article according to any one of the first to the sixteenth aspects, wherein the reinforcing fibers are reinforcing inorganic fibers.
- [0088] An eighteenth aspect of the invention is the article according to the seventeenth aspects, wherein the reinforcing inorganic fibers are selected from the group consisting of carbon fibers, basalts fibers and the combination thereof.
- [0089] A nineteenth aspect of the invention is the article according to the eighteenth aspects, wherein the reinforcing inorganic fibers are selected from the group consisting of carbon fibers and combinations thereof, preferably selected from the group consisting of ex-pitch carbon fibers, ex-PAN carbon fibers and combinations thereof.
- [0090] A twentieth aspect of the invention is the article according to any one of the first to the nineteenth aspects, wherein the ratio by weight of the reinforcing filler to the reinforcing fibers is less than 2.3 (for example, between 0.5 and 2.3), preferably less than 2.2 (for example, between 0.6 and 2.2).
- [0091] The rubber compositions of the contact element of the portion of the article according to the invention may be based on all or a part(s) of the usual additives generally used in the elastomer compositions for articles (for example, tires, shoes, conveyor or caterpillar tracks), such as, for example, protection agents, such as antiozone waxes, chemical antiozonants, antioxidants, tackifying resins, methylene acceptors (for example phenolic novolak resin), methylene donors (for example, hexamethylenetetramine (HMT), hexamethoxymethylmelamine (H3M) or combinations thereof), a crosslinking system (for examples, sulfur (sulphur), donors of sulfur, peroxide, bismaleimides, vulcanization accelerators, vulcanization activators or combinations thereof) or combinations thereof.
- [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 crosslinking system is preferably based on sulfur and on a primary vulcanization accelerator, in particular on an accelerator of sulfenamide type. Added to this vulcanization system are various known secondary accelerators or vulcanization activators, such as zinc oxide, stearic acid, guanidine derivatives (in particular diphenyl-

guanidine), and the like, incorporated during the first non-productive phase, during the productive phase or both. The content of sulfur is preferably between 0.5 and 10.0 phr, more preferably between 0.5 and 5.0 phr, still more preferably between 0.5 and 3.0 phr, and that of the primary accelerator is preferably between 0.5 and 5.0 phr.

[0094] 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 sulfur, in particular accelerators of the thiazoles type and their derivatives, accelerators of thiurams types, or zinc dithiocarbamates. These accelerators are more preferably selected from the group consisting of 2-mercaptobenzothiazyl disulfide (abbreviated to "MBTS"), N-cyclohexyl-2-benzothiazole sulfenamide (abbreviated to "CBS"), N,N-dicyclohexyl-2-benzothiazolesulfenamide ("DCBS"), N-tert-butyl-2-benzothiazolesulfenamide ("TBBS"), N-tert-butyl-2-benzothiazolesulfenimide ("TBSI"), zinc dibenzylthiocarbamate ("ZBEC"), Tetrabenzylthiuram disulfide ("TBZTD") and combinations thereof.

[0095] A twenty first aspect of the invention is the article according to any one of the first to the twentieth aspects, wherein the rubber composition is produced by a production method comprising at least at a step of incorporating at least the reinforcing fibers into the rubber composition in a mixer provided with at least two rolls having a roll nip which is equal to or more than the volume average length of reinforcing fibers before incorporating the reinforcing fibers into the rubber composition, wherein the volume average length of reinforcing fibers before incorporating the reinforcing fibers into the rubber composition is at least 1.0 mm (for example, from 1.0 to 15 mm) preferably at least 1.5 mm (for example, from 1.5 to 14 mm), more preferably at least 2.0 mm (for example, from 2.0 to 13 mm), still more preferably at least 2.5 mm (for example, from 2.5 to 12 mm), particularly at least 3.0 mm (for example, from 3.0 to 11 mm), more particular at least 3.5 mm (for example, from 3.5 to 10 mm). The meaning of roll(s) includes that of rotor(s). The roll nip is a distance of a gap between the rolls.

[0096] According to a preferred embodiment of the twenty first aspect, the step of incorporating at least the reinforcing fibers into the rubber composition occurs after incorporating the reinforcing filler into the rubber composition.

[0097] According to a more preferred embodiment of the twenty first aspect or the above preferred embodiment, the step of incorporating at least the reinforcing fibers into the rubber composition occurs after incorporating the plasticizing agent into the rubber composition.

[0098] According to a still more preferred embodiment of the twenty first aspect, the above preferred embodiment or the above more preferred embodiment, the rubber composition is further based on a crosslinking system, and the step of incorporating at least

the reinforcing fibers into the rubber composition occurs after incorporating the crosslinking system into the rubber composition.

- [0099] According to a particular embodiment of the twenty first aspect, the above preferred embodiment, the above more preferred embodiment or the above still more preferred embodiment, the roll nip is more than 1.0 mm, preferably more than 2.0 mm, more preferably more than 3.0 mm, still more preferably more than 4.0 mm, particularly more than 5.0 mm.
- [0100] According to a more particular embodiment of the twenty first aspect, the above preferred embodiment, the above more preferred embodiment, the above still more preferred embodiment or the above particular embodiment, the mixer is an internal mixer, for example, a Banbury mixer, a kneader, a Brabender.
- [0101] According to a still more particular embodiment of the above more particular embodiment, the internal mixer has a tip clearance which is equal to or above the volume average length of reinforcing fibers before incorporating the reinforcing fibers into the rubber composition. The tip clearance is a distance of a gap between the rotor and the wall of internal mixer.
- [0102] According to an advantageous embodiment of the above still more particular embodiment, the tip clearance is more than 1.0 mm, preferably more than 2.0 mm, more preferably more than 3.0 mm, still more preferably more than 4.0 mm, particularly more than 5.0 mm.
- [0103] According to a more advantageous embodiment of the above still more particular embodiment or the above advantageous embodiment, the internal mixer is filled with the composition for less than 65% (for example, between 45 and 65%) by volume of total volume of the mixer.
- [0104] Above the maximum indicated, there is to excessively enhance shear force to the composition in the mixer and that the shear force can make the reinforcing fibers shorter than the desired length.
- [0105] For all these reasons, it is preferably less than 60% (for example, between 50 and 60%) by volume of total volume of the mixer.
- [0106] According to another more particular embodiment of the twenty first aspect, the above preferred embodiment, the above more preferred embodiment, the above still more preferred embodiment or the above particular embodiment, the mixer is an external mixer, for example, an open roll mill.
- [0107] The rubber composition of the contact element of the portion of the article 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 system (vulcanization system) are incorporated.

[0108] According to an embodiment of the invention, a process which is 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 first mixer, the reinforcing filler, the plasticizing agent, the reinforcing fibers 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; and
- kneading everything up to a maximum temperature of less than 110°C.

[0109] According to a preferred embodiment of the invention, a process which is 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 first mixer, the reinforcing filler, the plasticizing agent, 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 and further the reinforcing fibers on a second mixer provided with at least two rolls having a roll nip which is a gap between the rolls and is equal to or more than the volume average length of reinforcing fibers; and
- kneading everything up to a maximum temperature of less than 110°C.

[0110] By way of example, the first (non-productive) phase is carried out in a single thermo-mechanical stage during which all the necessary constituents are introduced into an appropriate first 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.

[0111] After cooling the mixture thus obtained, the crosslinking system is then incorporated at low temperature (for example, between 40°C and 100°C), generally in an external

mixer as a second 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.

[0112] According to a more preferred embodiment of the preferred embodiment, the process comprises a step of each time maintaining the direction of introduction during the second (productive) phase in particular on the second mixer. That means the step that the rubber composition is reintroduced between the rolls by maintaining the direction of passage.

[0113] According to a still more preferred embodiment of the preferred embodiment or the more preferred embodiment, the process comprises a step of, during the second (productive) phase, incorporating the crosslinking system on the second mixer, subsequently, setting the roll nip of second mixer at equal to or more than the volume average length of reinforcing fibers before incorporating into the rubber composition, and then incorporating the reinforcing fibers on the second mixer.

[0114] According to another still more preferred embodiment of the preferred embodiment or the more preferred embodiment, the process comprises a step of, during the second (productive) phase, setting the roll nip of second mixer at equal to or more than the volume average length of reinforcing fibers before incorporating into the rubber composition, before incorporating the crosslinking system on the second mixer, and before incorporating the reinforcing fibers on the second mixer.

[0115] 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 can be used directly as an article, for example, a tire tread, a shoe sole, a conveyor belt and a caterpillar track tread.

[0116] Additionally, in order to prepare the form of the sheet or the plaque comprising the rubber composition comprising the reinforcing fibers extending substantially perpendicularly to the surface of the ground, it is possible to use any method known per se, notably as described for example in a patent application WO 2008/027045 filed by the application.

[0117] A twenty second aspect of the invention is the article according to any one of the first to the twenty first aspects, wherein $4.0 \geq S/H^2 \geq 0.1$, preferably $3.5 \geq S/H^2 \geq 0.2$, more preferably $3.0 \geq S/H^2 \geq 0.3$, still more preferably $2.5 \geq S/H^2 \geq 0.4$, particularly $2.0 \geq S/H^2 \geq 0.5$, more particularly $1.8 \geq S/H^2 \geq 0.6$, still more particularly $1.6 \geq S/H^2 \geq 0.7$.

[0118] A twenty third aspect of the invention is the article according to any one of the first to the twenty second aspects, wherein the height (H) (mm) of the contact element is less than 40 mm (for example, between 0 and 40 mm), preferably between less than 35 mm (for example, between 0 and 35 mm), more preferably between less than 30 mm (for example, between 0 and 30 mm), still more preferably less than 25 mm (for

example, between 0 and 25 mm).

- [0119] A twenty fourth aspect of the invention is the article according to any one of the first to the twenty third aspects, wherein the area (S) (mm²) of the contact surface is less than 1000 mm² (for example, between 10 and 1000 mm²), preferably less than 900 mm² (between 30 and 900 mm²), more preferably less than 800 mm² (for example, between 50 and 800 mm²), still more preferably less than 700 mm² (for example, between 70 and 700 mm²).
- [0120] A twenty fifth aspect of the invention is the article according to any one of the first to the twenty fourth aspects, wherein the contact surface of the contact element is substantially circular, and wherein its diameter (d) is between 5 and 35 mm, more preferably between 10 and 30 mm.
- [0121] The expression “substantially” circular means each diameter of the contact surface of the contact element is different from the average diameter of the contact surface of the contact element by less than 10%, preferably at most 5%, by length per 100% by length of the average diameter.
- [0122] A twenty sixth aspect of the invention is the article according to the twenty fifth aspect, wherein the contact element forms cylinder.
- [0123] The cylindrical contact element may be produced by rolling up the above sheet or the above plaque, which comprises the rubber composition comprising the reinforcing fibers extending substantially perpendicularly to the surface of the ground, in a direction substantially perpendicular to other directions to which the reinforcing fibers extend.
- [0124] 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 can 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.
- [0125] A twenty seventh aspect of the invention is the article according to any one of the first to the twenty sixth aspects, wherein the article is a tire, a shoe, a conveyor or a caterpillar track.
- [0126] According to a preferred embodiment of the twenty seventh aspect, the article is a shoe, preferably, the portion is comprised of a shoe sole, more preferably, the contact element is comprised of a block of a shoe sole.
- [0127] According to a preferred embodiment of the twenty seventh aspect, the article is a conveyor, preferably, the portion is comprised of a conveyor belt, more preferably, the contact element is comprised of a block of a conveyor belt.
- [0128] According to a preferred embodiment of the twenty seventh aspect, the article is a caterpillar track, preferably the portion is comprised of a caterpillar track tread, more

preferably, the contact element is comprised of a block of caterpillar track tread.

[0129] A twenty eighth aspect of the invention is the article according to the twenty seventh aspect, wherein the article is a tire.

[0130] According to a preferred embodiment of the twenty eighth aspect, the tire is particularly intended to be equipped to passenger motor vehicles, including 4×4 (four-wheel drive) vehicles and SUV (Sport Utility Vehicles) vehicles, and also industrial vehicles in particular chosen from vans and heavy duty vehicles (i.e., bus or heavy road transport vehicles (lorries, tractors, trailers)).

[0131] A twenty ninth aspect of the invention is the article according to the twenty eighth aspect, wherein the portion is comprised of a tread of a tire.

[0132] According to a preferred embodiment of the twenty ninth aspect, the portion is a cap-tread(s), a sub-tread(s) or the both of the tire. Each of them is intended to come into contact with the ground during the service life of the tire, and the cap-tread(s) is intended to come into contact with the ground prior to the sub-tread(s), that is, the cap-tread(s) is positioned radially outer than the sub-tread(s) in the tire.

[0133] A thirtieth aspect of the invention is the article according to the twenty ninth aspect, wherein the contact element is comprised of a block of a tread of a tire.

[0134] The invention relates to the rubber compositions and the above articles, both in the mixed state (after mixing and before curing) and in the cured state (i.e., after crosslinking or vulcanization).

[0135] The invention is further illustrated by the following non-limiting examples.

Example

[0136] Thirty nine test specimens (identified as T-1 (a reference), T-2, T-3, T-12 to T-17, T-26 to T-30 and T-39 (comparative examples), T-4 to T-11, T-18 to T-25, T-31 to T-38 (examples according to the invention)) comprising rubber compositions were tested. The formulations of the rubber compositions with the content of the various products expressed in phr are given at Tables 1 to 6.

[0137] Each rubber composition, except T-1, T-2, T-13, T-15, T-16 T-27, T-29 and T-30, was produced as follows: The reinforcing filler, its associated coupling agent, the elastomer matrix, the plasticizing agent and the various other ingredients, furthermore the reinforcing fibers in T-3, T-4, T-17, T-18 and T-31 only, with the exception of the vulcanization system, were successively introduced into an internal mixer having an initial vessel temperature of approximately 80°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 5 to 6 minutes, until a maximum “dropping” temperature of around 160°C (150 to 165°C) was reached. The mixture thus obtained was recovered and cooled, and then sulfur and an accelerator of sulfenamide type, furthermore the reinforcing fibers in all of the examples (other than

T-4, T-18 and T-31) according to the invention, were incorporated on an external mixer (homofinisher), which was an open mill having two rolls of which the nip was set at 1.0, 2.0 or 4.0 mm, at 20 to 50°C, everything being mixed (productive phase) for an appropriate time (for example, between 5 and 12 min) up to a maximum temperature of the combine mixture of 40 to 100°C. This operation to homogenize the vulcanization system (sulfur and sulfenamide) and to orient the reinforcing fibers to the same direction consisted in passing the compound between the rolls several times, each time maintaining the direction of introduction (the compound was recovered under the rolls, it was reintroduced between the rolls by maintaining the direction of passage).

[0138] The roll nip was above the volume average length of reinforcing fibers in the cured state, and was equal to the volume average length of reinforcing fibers before the reinforcing fibers were mixed with the other ingredients of each rubber composition. Thus, it was sure that the roll nip was equal to or more than the volume average length of reinforcing fibers in the mixed state, of course, and in the cured state.

[0139] The rubber compositions thus obtained were subsequently calendered by a third device, either in the form of sheets (thickness of 2 to 3 mm) or fine sheets of rubber, and the rubber sheets were cut in a direction substantially perpendicular to the above direction of passage between the rolls. It was observed by an optical microscope mentioned below that the reinforcing fibers appearing on the surfaces of sheets were oriented in a direction substantially perpendicular to the above cutting direction. Each of the above cutting sheets was rolled up in a direction substantially perpendicular to the cutting direction, and each cylindrical block as each test specimen was obtained. Each of the cylindrical blocks had each height (H) (mm), each circular contact surface with each diameter (d) (mm), and each area (S) (mm²) of the contact surface shown in Tables 1 to 6. The cylindrical blocks of the examples (T-4 to T-11, T-18 to T-25, T-31 to T-38) can be a contact element of a portion of an article according to the invention.

[0140] Each of the other specimens (T-1, T-2, T-13, T-15, T-16 T-27, T-29 and T-30) was produced by the same process without incorporating reinforcing fibers into each rubber composition

[0141] After molding into the blocks and before the following measurements/tests, each of them was placed in a press with heated platens at a temperature (typically 150°C), and for the time that was necessary for the crosslinking of these rubber compositions (typically several tens of minutes), at a pressure (typically 16 bar).

[0142] The length (and the diameter also if necessary) of each reinforcing fiber in the rubber compositions of the test specimens (with the reinforcing fibers) in the cured state was measured in accordance with the procedure described below in several steps. The object formed by the rubber composition after compounding the constituents of the rubber composition and after mixed, preferably after vulcanization, that is cured state,

is referred to as a compound.

[0143] The first step consisted in extracting the reinforcing fibers from the compound by proceeding in the following manner:

- the compound was cut into small pieces then an acetone extraction was carried out so as to eliminate as much as possible the plasticizing agent (for example, oil(s), resin(s)), and the additives such waxes, and antioxidants, described below;
- the compound was then pyrolysed under an inert atmosphere (N₂) at 550°C, so as to eliminate the organic substances by cracking: polymers, sulfur network, accelerators, residual plasticizing agent, described below;
- the residue obtained then contained the reinforcing fibers, the reinforcing filler (the reinforcing inorganic filler, carbon black or both) and mineral products initially present in the compound (such as silica) or optionally formed during the pyrolysis.

[0144] The second step consisted in preparing the sample to be placed in a microscope by proceeding in the following manner:

- At the end of the first step, the combustion residues containing the reinforcing fibers were recovered. These residues were very slightly compressed using a mortar and pestle in order to separate the fibers from one another.
- The reinforcing fibers were thus recovered on a sample holder comprising a carbon adhesive tape. It was also possible to directly stamp the aluminum sample holder bearing the carbon adhesive tape onto the extracted fibers.
- The samples were then blown with dry air in order to eliminate the free fibers that could damage the column of the microscope.

[0145] The third step consisted in determining the dimensions of the reinforcing fibers:

- The samples were observed by a microscopy on the microscope which is an optical microscope (VCR-800 from HiROX Co., Ltd.). Also, the microscopy can be on a scanning electron microscope (SEM).
- For each sample, lengths and diameters of at least 100 objects (reinforcing fibers) extracted from each compound, which was each of these rubber compositions (T-3, T-4, C-1, C-2 and C-3), were measured.
- Each number average of the reinforcing fibers and each volume average of the reinforcing fibers in the cured state were calculated with the above measurement results.

[0146] By the above third step, the length (and the diameter) and the number average, and the volume average of reinforcing fibers before incorporating the reinforcing fibers into the rubber composition was also measured and calculated.

[0147] Each of the test specimens was placed between two metallic platens in an INSTRON testing machine of type 5969, and was compressed in a direction of the thickness of each of the test specimens, at a rate of 10 mm/min after done, 3 times or more, the following step which was that each of the specimens was compressed from 0 to 50 %

of the compressive strain (= compressive deflection / initial thickness of the test specimens) at a rate of 10 mm/min, and then was released from 50 to 0% of the compressive strain at a rate of 10 min/min. The INSTRON machine was used to record each compressive force versus compressive deflection as first results.

[0148] The first results and the initial sizes of the specimens were used to calculate each compressive stress (= compressive force / the area of the contact surface of the test specimens) versus compressive strain (= compressive deflection / initial thickness of the test specimens) as second results.

[0149] The second results were used to compute each criterion value (Compression modulus at 5% [MPa] (= “the compressive stress at which the compressive strain is 5%” / 5%), Compression modulus at 20% [MPa] (= “the compressive stress at which the compressive strain is 20%” / 20%), and Ratio of the compression modulus at 20% to the compression modulus at 5%) for each of the test specimens.

[0150] “Compression modulus at 5%” is representative of the load supporting function of the article, therefore the compression modulus greater than that of the reference indicates improved the function.

[0151] “Ratio of Compression modulus at 20% to Compression modulus at 5%” is representative of the shock absorption function of the article, therefore the compression modulus less than that of the reference and the ratio less than 0.45 indicates improved the function.

[0152] The results from Tables 1 to 6 demonstrate that the test specimens according to the invention have unexpectedly improved the balance of the load supporting function and the shock absorption function than that of the reference.

[0153] In conclusion, the contact element of the portion of the article according to the invention allows unexpectedly improved the balance of the load supporting function and the shock absorption function of the article.

[0154]

[Table 1]

	T-1	T-2	T-3	T-4	T-5	T-6	T-7
SBR (1) [phr]	80	80	80	80	80	80	80
BR (2) [phr]	20	20	20	20	20	20	20
NR (3) [phr]							
Carbon black (4) [phr]	3	3	3	3	3	3	3
Silica (5) [phr]	110	30	110	30	30	30	30
Coupling agent (6) [phr]	8.8	2.4	8.8	2.4	2.4	2.4	2.4
Liquid plasticizer 1(7) [phr]	15	20	15	20	20	20	20
Liquid plasticizer 2(8) [phr]							
Hydrocarbon resin (9) [phr]	55	80	55	80	80	80	80
Reinforcing fiber 1 (10) [phr]			48.0	48.0			
Reinforcing fiber 2 (11) [phr]					48.0		
Reinforcing fiber 3 (12) [phr]						48.0	
Reinforcing fiber 4 (13) [phr]							48.0
Antioxidant (14) [phr]	4.4	4.4	4.4	4.4	4.4	4.4	4.4
Antiozone wax [phr]	2	2	2	2	2	2	2
DPG (15) [phr]	2	2	2	2	2	2	2
Stearic acid [phr]	2	2	2	2	2	2	2
Zinc oxide [phr]	1	1	1	1	1	1	1
Sulphur [phr]	1	1	1	1	1	1	1
CBS (16) [phr]	2.3	2.3	2.3	2.3	2.3	2.3	2.3
Ratio by weight of the plasticizing agent to the reinforcing filler	0.63	3.03	0.63	3.03	3.03	3.03	3.03
Ratio by weight of the hydrocarbon resin to the liquid plasticizer	3.67	4.00	3.67	4.00	4.00	4.00	4.00
Ratio by weight of the reinforcing filler to the reinforcing fibers			2.35	0.69	0.69	0.69	0.69
H: Height of the block specimen [mm]	20	20	20	20	20	20	20
D: Diameter of circle of contact surface of the block specimen [mm]	9.5	9.5	9.5	9.5	9.5	9.5	9.5
S: Area of contact surface of the block specimen [mm ²]	71	71	71	71	71	71	71
S/H ²	0.18	0.18	0.18	0.18	0.18	0.18	0.18
Compression modulus at 5% [MPa]	4.10	1.11	10.55	4.11	4.49	4.64	5.30
Ratio of compression modulus at 20% to compression modulus at 5%	0.97	1.11	0.61	0.32	0.35	0.42	0.39

[0155]

[Table 2]

	T-8	T-9	T-10	T-11	T-12	T-13	T-14
SBR (1) [phr]	80	80	80	80	80		
BR (2) [phr]	20	20	20	20	20	40	40
NR (3) [phr]						60	60
Carbon black (4) [phr]	3	3	3	3	3	45	45
Silica (5) [phr]	30	30	30	30	30	20	20
Coupling agent (6) [phr]	2.4	2.4	2.4	2.4	2.4	1.2	1.2
Liquid plasticizer 1(7) [phr]	20	20	20	20	20		
Liquid plasticizer 2(8) [phr]						20	20
Hydrocarbon resin (9) [phr]	80	80	80	80	80		
Reinforcing fiber 1 (10) [phr]							
Reinforcing fiber 2 (11) [phr]							
Reinforcing fiber 3 (12) [phr]							
Reinforcing fiber 4 (13) [phr]	37.5	30.0	22.7	15.7	8.8		15.7
Antioxidant (14) [phr]	4.4	4.4	4.4	4.4	4.4		
Antiozone wax [phr]	2	2	2	2	2	2	2
DPG (15) [phr]	2	2	2	2	2		
Stearic acid [phr]	2	2	2	2	2	2	2
Zinc oxide [phr]	1	1	1	1	1	3	3
Sulphur [phr]	1	1	1	1	1	1.5	1.5
CBS (16) [phr]	2.3	2.3	2.3	2.3	2.3	1	1
Ratio by weight of the plasticizing agent to the reinforcing filler	3.03	3.03	3.03	3.03	3.03	0.31	0.31
Ratio by weight of the hydrocarbon resin to the liquid plasticizer	4.00	4.00	4.00	4.00	4.00		
Ratio by weight of the reinforcing filler to the reinforcing fibers	0.88	1.10	1.45	2.10	3.75		4.14
H: Height of the block specimen [mm]	20	20	20	20	20	20	20
D: Diameter of circle of contact surface of the block specimen [mm]	9.5	9.5	9.5	9.5	9.5	9.5	9.5
S: Area of contact surface of the block specimen [mm ²]	71	71	71	71	71	71	71
S/H ²	0.18	0.18	0.18	0.18	0.18	0.18	0.18
Compression modulus at 5% [MPa]	5.25	4.84	4.43	4.20	2.50	4.20	10.0
Ratio of compression modulus at 20% to compression modulus at 5%	0.40	0.38	0.40	0.30	0.50	0.86	0.46

[0156]

[Table 3]

	T-15	T-16	T-17	T-18	T-19	T-20	T-21
SBR (1) [phr]	80	80	80	80	80	80	80
BR (2) [phr]	20	20	20	20	20	20	20
NR (3) [phr]							
Carbon black (4) [phr]	3	3	3	3	3	3	3
Silica (5) [phr]	110	30	110	30	30	30	30
Coupling agent (6) [phr]	8.8	2.4	8.8	2.4	2.4	2.4	2.4
Liquid plasticizer 1(7) [phr]	15	20	15	20	20	20	20
Liquid plasticizer 2(8) [phr]							
Hydrocarbon resin (9) [phr]	55	80	55	80	80	80	80
Reinforcing fiber 1 (10) [phr]			48.0	48.0			
Reinforcing fiber 2 (11) [phr]					48.0		
Reinforcing fiber 3 (12) [phr]						48.0	
Reinforcing fiber 4 (13) [phr]							48.0
Antioxidant (14) [phr]	4.4	4.4	4.4	4.4	4.4	4.4	4.4
Antiozone wax [phr]	2	2	2	2	2	2	2
DPG (15) [phr]	2	2	2	2	2	2	2
Stearic acid [phr]	2	2	2	2	2	2	2
Zinc oxide [phr]	1	1	1	1	1	1	1
Sulphur [phr]	1	1	1	1	1	1	1
CBS (16) [phr]	2.3	2.3	2.3	2.3	2.3	2.3	2.3
Ratio by weight of the plasticizing agent to the reinforcing filler	0.63	3.03	0.63	3.03	3.03	3.03	3.03
Ratio by weight of the hydrocarbon resin to the liquid plasticizer	3.67	4.00	3.67	4.00	4.00	4.00	4.00
Ratio by weight of the reinforcing filler to the reinforcing fibers			2.35	0.69	0.69	0.69	0.69
H: Height of the block specimen [mm]	20	20	20	20	20	20	20
D: Diameter of circle of contact surface of the block specimen [mm]	19	19	19	19	19	19	19
S: Area of contact surface of the block specimen [mm ²]	284	284	284	284	284	284	284
S/H ²	0.71	0.71	0.71	0.71	0.71	0.71	0.71
Compression modulus at 5% [MPa]	4.62	1.28	11.28	5.25	5.68	6.37	8.08
Ratio of compression modulus at 20% to compression modulus at 5%	0.90	0.63	0.58	0.40	0.43	0.41	0.39

[0157]

[Table 4]

	T-22	T-23	T-24	T-25	T-26	T-27	T-28
SBR (1) [phr]	80	80	80	80	80		
BR (2) [phr]	20	20	20	20	20	40	40
NR (3) [phr]						60	60
Carbon black (4) [phr]	3	3	3	3	3	45	45
Silica (5) [phr]	30	30	30	30	30	20	20
Coupling agent (6) [phr]	2.4	2.4	2.4	2.4	2.4	1.2	1.2
Liquid plasticizer 1(7) [phr]	20	20	20	20	20		
Liquid plasticizer 2(8) [phr]						20	20
Hydrocarbon resin (9) [phr]	80	80	80	80	80		
Reinforcing fiber 1 (10) [phr]							
Reinforcing fiber 2 (11) [phr]							
Reinforcing fiber 3 (12) [phr]							
Reinforcing fiber 4 (13) [phr]	37.5	30.0	22.7	15.7	8.8		15.7
Antioxidant (14) [phr]	4.4	4.4	4.4	4.4	4.4		
Antiozone wax [phr]	2	2	2	2	2	2	2
DPG (15) [phr]	2	2	2	2	2		
Stearic acid [phr]	2	2	2	2	2	2	2
Zinc oxide [phr]	1	1	1	1	1	3	3
Sulphur [phr]	1	1	1	1	1	1.5	1.5
CBS (16) [phr]	2.3	2.3	2.3	2.3	2.3	1	1
Ratio by weight of the plasticizing agent to the reinforcing filler	3.03	3.03	3.03	3.03	3.03	0.31	0.31
Ratio by weight of the hydrocarbon resin to the liquid plasticizer	4.00	4.00	4.00	4.00	4.00		
Ratio by weight of the reinforcing filler to the reinforcing fibers	0.88	1.10	1.45	2.10	3.75		4.14
H: Height of the block specimen [mm]	20	20	20	20	20	20	20
D: Diameter of circle of contact surface of the block specimen [mm]	19	19	19	19	19	19	19
S: Area of contact surface of the block specimen [mm ²]	284	284	284	284	284	284	284
S/H ²	0.71	0.71	0.71	0.71	0.71	0.71	0.71
Compression modulus at 5% [MPa]	7.04	6.90	5.34	5.26	3.54	4.46	12.6
Ratio of compression modulus at 20% to compression modulus at 5%	0.38	0.38	0.43	0.38	0.51	0.87	0.48

[0158]

[Table 5]

	T-29	T-30	T-31	T-32	T-33	T-34
SBR (1) [phr]	80	80	80	80	80	80
BR (2) [phr]	20	20	20	20	20	20
NR (3) [phr]						
Carbon black (4) [phr]	3	3	3	3	3	3
Silica (5) [phr]	110	30	30	30	30	30
Coupling agent (6) [phr]	8.8	2.4	2.4	2.4	2.4	2.4
Liquid plasticizer 1(7) [phr]	15	20	20	20	20	20
Liquid plasticizer 2(8) [phr]						
Hydrocarbon resin (9) [phr]	55	80	80	80	80	80
Reinforcing fiber 1 (10) [phr]			48.0			
Reinforcing fiber 2 (11) [phr]				48.0		
Reinforcing fiber 3 (12) [phr]					48.0	
Reinforcing fiber 4 (13) [phr]						48.0
Antioxidant (14) [phr]	4.4	4.4	4.4	4.4	4.4	4.4
Antiozone wax [phr]	2	2	2	2	2	2
DPG (15) [phr]	2	2	2	2	2	2
Stearic acid [phr]	2	2	2	2	2	2
Zinc oxide [phr]	1	1	1	1	1	1
Sulphur [phr]	1	1	1	1	1	1
CBS (16) [phr]	2.3	2.3	2.3	2.3	2.3	2.3
Ratio by weight of the plasticizing agent to the reinforcing filler	0.63	3.03	3.03	3.03	3.03	3.03
Ratio by weight of the hydrocarbon resin to the liquid plasticizer	3.67	4.00	4.00	4.00	4.00	4.00
Ratio by weight of the reinforcing filler to the reinforcing fibers			0.69	0.69	0.69	0.69
H: Height of the block specimen [mm]	20	20	20	20	20	20
D: Diameter of circle of contact surface of the block specimen [mm]	28	28	28	28	28	28
S: Area of contact surface of the block specimen [mm ²]	616	616	616	616	616	616
S/H ²	1.54	1.54	1.54	1.54	1.54	1.54
Compression modulus at 5% [MPa]	5.24	1.42	5.84	6.23	7.25	8.98
Ratio of compression modulus at 20% to compression modulus at 5%	0.88	1.06	0.38	0.43	0.41	0.38

[0159]

[Table 6]

	T-35	T-36	T-37	T-38	T-39
SBR (1) [phr]	80	80	80	80	80
BR (2) [phr]	20	20	20	20	20
NR (3) [phr]					
Carbon black (4) [phr]	3	3	3	3	3
Silica (5) [phr]	30	30	30	30	30
Coupling agent (6) [phr]	2.4	2.4	2.4	2.4	2.4
Liquid plasticizer 1(7) [phr]	20	20	20	20	20
Liquid plasticizer 2(8) [phr]					
Hydrocarbon resin (9) [phr]	80	80	80	80	80
Reinforcing fiber 1 (10) [phr]					
Reinforcing fiber 2 (11) [phr]					
Reinforcing fiber 3 (12) [phr]					
Reinforcing fiber 4 (13) [phr]	37.5	30.0	22.7	15.7	8.8
Antioxidant (14) [phr]	4.4	4.4	4.4	4.4	4.4
Antiozone wax [phr]	2	2	2	2	2
DPG (15) [phr]	2	2	2	2	2
Stearic acid [phr]	2	2	2	2	2
Zinc oxide [phr]	1	1	1	1	1
Sulphur [phr]	1	1	1	1	1
CBS (16) [phr]	2.3	2.3	2.3	2.3	2.3
Ratio by weight of the plasticizing agent to the reinforcing filler	3.03	3.03	3.03	3.03	3.03
Ratio by weight of the hydrocarbon resin to the liquid plasticizer	4.00	4.00	4.00	4.00	4.00
Ratio by weight of the reinforcing filler to the reinforcing fibers	0.88	1.10	1.45	2.10	3.75
H: Height of the block specimen [mm]	20	20	20	20	20
D: Diameter of circle of contact surface of the block specimen [mm]	28	28	28	28	28
S: Area of contact surface of the block specimen [mm ²]	616	616	616	616	616
S/H ²	1.54	1.54	1.54	1.54	1.54
Compression modulus at 5% [MPa]	7.72	6.26	6.04	5.25	3.73
Ratio of compression modulus at 20% to compression modulus at 5%	0.40	0.43	0.41	0.40	0.51

(1) SBR: Solution SBR with 27% of styrene unit ($T_{gDSC} = -48^{\circ}\text{C}$);

(2) BR: BR with 0.3% of 1,2 vinyl; 2.7% of trans; 97% of cis-1,4 ($T_{gDSC} = -105^{\circ}\text{C}$);

- (3) NR: Natural rubber (peptised);
- (4) Carbon black: Carbon black (ASTM grade N234 from Cabot);
- (5) Silica: Silica ("Zeosil 1165MP" from Rhodia (CTAB, BET: 160 m²/g));
- (6) Coupling agent TESPT ("Si69" from Evonik);
- (7) Oleic sunflower oil ("Agripure 80" from Cargill, Weight percent oleic acid: 100%);
- (8) MES oil ("Catenex SNR" from Shell);
- (9) Cycloaliphatic hydrocarbon resins ("ESCOREZ5600" from ExxonMobil, T_{gDSC} = 52°C);
- (10) Carbon fibers, as reinforcing fibers, covered with resorcinol formaldehyde latex glue (from Nippon Sheet Glass Co., Ltd.), having a volume average length of 1.0 mm before incorporating the reinforcing fibers into each rubber composition, the reinforcing fibers having a diameter of 8μm before incorporating the reinforcing fibers into each rubber composition, the reinforcing fibers incorporated with the other ingredient of each rubber composition, with the exception of the crosslinking system, into each rubber composition in the internal mixer by a conventional process, and the reinforcing fibers having a volume average length of 0.2 mm in the cured state;
- (11) Carbon fibers, as reinforcing fibers, covered with resorcinol formaldehyde latex glue (from Nippon Sheet Glass Co., Ltd.), having a volume average length of 1.0 mm before incorporating the reinforcing fibers into each rubber composition, the reinforcing fibers having a diameter of 8μm before incorporating the reinforcing fibers into each rubber composition, the reinforcing fibers incorporated with the crosslinking system, after incorporating the other ingredients of each rubber composition, into each rubber composition on the roll nip of 1.0 mm, and the reinforcing fiber having a volume average length of 0.9 mm in the cured state;
- (12) Carbon fibers, as reinforcing fibers, covered with resorcinol formaldehyde latex glue (from Nippon Sheet Glass Co., Ltd.), having a volume average length of 2.0 mm before incorporating the reinforcing fibers into each rubber composition, the reinforcing fibers having a diameter of 8μm before incorporating the reinforcing fibers into each rubber composition, the reinforcing fibers incorporated with the crosslinking system, after incorporating the other ingredients of each rubber composition, into each rubber composition on the roll nip of 2.0 mm, and the reinforcing fiber having a volume average length of 1.9 mm in the cured state;
- (13) Carbon fibers, as reinforcing fibers, covered with resorcinol formaldehyde latex glue (from Nippon Sheet Glass Co., Ltd.), having a volume average length of 4.0 mm before incorporating the reinforcing fibers into each rubber composition, the reinforcing fibers having a diameter of 8μm before incorporating the reinforcing fibers into each rubber composition, the reinforcing fibers incorporated with the crosslinking system, after incorporating the other ingredients of each rubber composition, into each

rubber composition on the roll nip of 4.0 mm, and the reinforcing fiber having a volume average length of 3.9 mm in the cured state;

(14) Mixture of N-(1,3-dimethylbutyl)-N-phenyl-para-phenylenediamine (“Santoflex 6-PPD” from Flexsys) and 2,2,4-trimethyl-1,2-dihydroquinolone (“TMQ” from Lanxess);

(15) Diphenylguanidine (“Perkacit DPG” from Flexsys);

(16) N-dicyclohexyl-2-benzothiazolesulfenamide (“Santocure CBS” from Flexsys);

Claims

- [Claim 1] An article comprising a portion comprising a contact element having a height (H) (mm), a contact surface intended to come into contact with the ground, and an area (S) (mm²) of the contact surface, the contact element comprising a rubber composition based on at least an elastomer matrix, a reinforcing filler, a plasticizing agent, and more than 10 phr of reinforcing fibers extending substantially perpendicularly to the surface of the ground; wherein a ratio by weight of the plasticizing agent to the reinforcing filler is more than 1.0.
- [Claim 2] The article according to Claim 1, wherein the elastomer matrix comprises at least one diene elastomer selected from natural rubber, synthetic polyisoprenes, polybutadienes, butadiene copolymers, isoprene copolymers and combinations thereof.
- [Claim 3] The article according to Claim 1 or Claim 2, wherein the elastomer matrix comprises more than 50 phr of a first diene elastomer which is a styrene-butadiene copolymer, and optionally comprises less than 50 phr of a second diene elastomer which is different from the first diene elastomer.
- [Claim 4] The article according to any one of Claims 1 to 3, wherein the amount of reinforcing filler is less than 65 phr.
- [Claim 5] The article according to any one of Claims 1 to 4, wherein the reinforcing filler predominately comprises a reinforcing inorganic filler.
- [Claim 6] The article according to Claim 5, wherein the reinforcing inorganic filler predominantly comprises silica.
- [Claim 7] The article according to any one of Claims 1 to 6, wherein the reinforcing filler comprises less than 20 phr of carbon black.
- [Claim 8] The article according to any one of Claims 1 to 7, wherein the amount of plasticizing agent is more than 70 phr.
- [Claim 9] The article according to any one of Claims 1 to 8, wherein the ratio by weight of the plasticizing agent to the reinforcing filler is more than 1.5.
- [Claim 10] The article according to any one of Claims 1 to 9, wherein the plasticizing agent is selected from the group consisting of liquid plasticizer(s), hydrocarbon resin(s) and combinations thereof.
- [Claim 11] The article according to Claim 10, wherein a ratio by weight of the hydrocarbon resin(s) to the liquid plasticizer(s) is more than 0.5.

- [Claim 12] The article according to any one of Claims 1 to 11, wherein the amount of reinforcing fibers is more than 15 phr.
- [Claim 13] The article according to any one of Claims 1 to 12, wherein the volume average length of reinforcing fibers is at least 1.0 mm before incorporating the reinforcing fibers into the rubber composition.
- [Claim 14] The article according to any one of Claims 1 to 13, wherein the volume average length of reinforcing fibers is more than 0.5 mm in the mixed state.
- [Claim 15] The article according to any one of Claims 1 to 14, wherein the volume average length of reinforcing fibers is more than 0.5 mm in the cured state.
- [Claim 16] The article according to any one of Claims 1 to 15, wherein the reinforcing fibers are covered with glue.
- [Claim 17] The article according to any one of Claims 1 to 16, wherein the reinforcing fibers are reinforcing inorganic fibers.
- [Claim 18] The article according to Claim 17, wherein the reinforcing inorganic fibers are selected from the group consisting of carbon fibers, basalts fibers and the combination thereof.
- [Claim 19] The article according to Claim 18, wherein the reinforcing inorganic fibers are selected from the group consisting of carbon fibers and combinations thereof.
- [Claim 20] The article according to any one of Claims 1 to 19, wherein the ratio by weight of the reinforcing filler to the reinforcing fibers is less than 2.3.
- [Claim 21] The article according to any one of Claims 1 to 20, wherein the rubber composition is produced by a production method comprising at least at a step of incorporating at least the reinforcing fibers into the rubber composition in a mixer provided with at least two rolls having a roll nip which is equal to or above the volume average length of reinforcing fibers before incorporating the reinforcing fibers into the rubber composition, wherein the volume average length of reinforcing fibers before incorporating the reinforcing fibers into the rubber composition is at least 1.0 mm.
- [Claim 22] The article according to any one of Claims 1 to 21, wherein $4.0 \geq S/H^2 \geq 0.1$.
- [Claim 23] The article according to any one of Claims 1 to 22, wherein the height (H) (mm) of the contact element is less than 40 mm.
- [Claim 24] The article according to any one of Claims 1 to 23, wherein the area (S) (mm²) of the contact surface is less than 1000 mm².

- [Claim 25] The article according to any one of Claims 1 to 24, wherein the contact surface of the contact element is substantially circular, and wherein its diameter (d) is between 5 and 35 mm.
- [Claim 26] The article according to Claim 25, wherein the contact element is cylindrical.
- [Claim 27] The article according to any one of Claims 1 to 26, wherein the article is a tire, a shoe, a conveyor or a caterpillar track.
- [Claim 28] The article according to Claim 27, wherein the article is a tire.
- [Claim 29] The article according to Claim 28, wherein the portion is comprised of a tread of a tire.
- [Claim 30] The article according to Claim 29, wherein the contact element is comprised of a block of a tread of a tire.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER INV. B60C1/00 C08L7/00 C08K7/02 C08L9/06 C08K3/36 ADD.		
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) C08K B60C C08L A43B B65G		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2013/087878 A1 (MICHELIN & CIE [FR]; MICHELIN RECH TECH [CH]) 20 June 2013 (2013-06-20) essais A2-A5; table 1 figures 1-2	1-30
A	WO 2016/104815 A1 (MICHELIN & CIE [FR]; MICHELIN RECH TECH [CH] ET AL.) 30 June 2016 (2016-06-30) claims example C4 paragraph [0113]	1-30
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "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 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
21 February 2020		13/03/2020
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Baekelmans, Didier

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 676 878 A1 (GOODYEAR TIRE & RUBBER [US]) 5 July 2006 (2006-07-05) paragraph [0001] claims 1-3 table 1 paragraph [0022] -----	1-30

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