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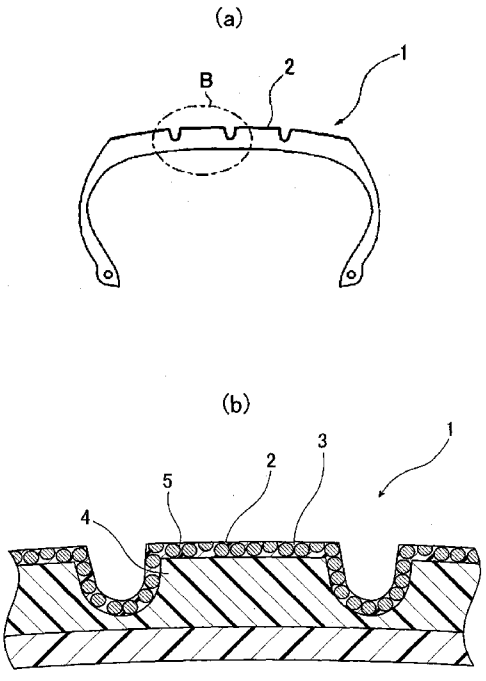
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[Continued on next page]

(54) Title: A PNEUMATIC TIRE HAVING A TREAD COMPRISING MILLIPARTICLES

FIG.1



(57) Abstract: A pneumatic tire having a tread suitable for a winter tires, having a high grip on snow/ice, the pneumatic tire having the tread comprising at least two radially superposed portions. Such a tread is comprising a surfacic portion intended to come into contact with ground during rolling at least when the tread is new and in the cured state, having a thickness of more than 1 mm and being made of a rubber composition, an internal portion adjacent to the surfacic portion, having a thickness of more than 1 mm and being made of a rubber composition which is different from the rubber composition of the surfacic portion. The rubber composition of the surfacic portion comprises at least a diene elastomer, more than 30 phr of a liquid plasticizer, 50 to 150 phr of a reinforcing filler and milliparticles having a median size by weight of more than 1 mm, and a volume fraction of the milliparticles more than 20% in volume of the rubber composition of the surfacic portion.

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DESCRIPTION

Title of Invention

A PNEUMATIC TIRE HAVING A TREAD COMPRISING MILLIPARTICLES

【0001】

1. FIELD OF THE INVENTION

The invention relates to a pneumatic tire having a tread suitable for "winter tires" capable of rolling over ground surfaces covered with snow and/or ice without being provided with studs (also known as studless tires). It relates more particularly to a pneumatic tire having a tread having a composite structure with a least a surface portion and an internal portion which are radially adjacent and have different formulations.

【0002】

2. BACKGROUND

In order to ensure performance of tire tread on snow and/or ice, it is well known that creation of microroughness on tread surface is a convenient way. This can be achieved by introduction of many types of microparticles inside rubber composition(s).

【0003】

For instance, patent applications JP 05/287130, WO 2009/083125, WO 2010/009850, WO 2011/073186, WO 2011/086061, WO2012/052331 and WO 2012/085063 filed

by the applicants described specific rubber compositions which are capable of generating an effective surface microroughness by virtue of microparticles having a median size by weight of 1 mm or less and which makes it possible to improve grip on ice of the treads and tires comprising them under melting ice conditions encountered within a temperature range typically of between -5°C and 0°C.

【0004】

However, when the said microparticles create microcavities after gradual expulsion from the rubber matrix, grip on snow of tread and tire is not improved especially under compacted snow which can be commonly found on roads in winter.

【0005】

3. BRIF DESCRIPTION OF THE INVENTION

On continuing their research, the applicants have discovered a novel and specific surfacic portion of a tread of a pneumatic tire, the surfacic portion comprising a rubber composition which is capable of generating a well-known "claw effect" on snow surface (of course, on ice surface too) by virtue of milliparticles before releasing millicavities, and then, subsequently, after gradual expulsion from the rubber composition, the milliparticles release the millicavities substantially scraping, picking up and retaining snow from the ground and then efficiently leading higher friction coefficient than normal friction coefficient between snow and rubber and which makes possible an improvement of grip on snow of tires comprising this tread.

【0006】

The millicavities act as storage volume and as channel for draining water or water film layer on snow or ice surfaces, the water or the water film layer being generated

by pressure of the tires during passage of a vehicle; under these conditions, the contact between the surface of the tread and snow or ice is no longer lubricated and the coefficient of friction is thus improved.

【0007】

Thus, a first subject matter of the invention is a pneumatic tire having a tread comprising at least two radially superposed portions comprising;

- a surfacic portion intended to come into contact with ground during rolling at least when the tread is new (or before use) and in the cured state, having a thickness of more than 1 mm and being made of a rubber composition,

-an internal portion adjacent to the surfacic portion, having a thickness of more than 1 mm and being made of a rubber composition which is different from the rubber composition of the surfacic portion,

wherein the rubber composition of the surfacic portion comprises at least;

- a diene elastomer;
- more than 30 phr of a liquid plasticizer;
- 50 to 150 phr of a reinforcing filler; and
- milliparticles having a median size by weight of more than 1 mm, and a volume fraction of the milliparticles more than 20% in volume of the rubber composition of the surfacic portion.

【0008】

Moreover, aspects of the invention can be as follows.

[1] A pneumatic tire having a tread comprising at least two radially superposed portions comprising:

- a surfacic portion intended to come into contact with ground during rolling at least when the tread is new and in the cured state, having a thickness of more than 1 mm and being made of a rubber composition,

- an internal portion adjacent to the surfacic portion, having a thickness of more than 1 mm and being made of a rubber composition which is different from the rubber composition of the surfacic portion,

wherein the rubber composition of the surfacic portion comprises at least:

- a diene elastomer;
- more than 30 phr of a liquid plasticizer;
- 50 to 150 phr of a reinforcing filler; and
- milliparticles having a median size by weight of more than 1 mm, in a volume fraction of the milliparticles of more than 20% in volume of the rubber composition of the surfacic portion.

【0009】

[2] The tire according to [1], wherein the volume fraction of the milliparticles is more than 30% in volume of the rubber composition of the surfacic portion.

[3] The tire according to [1] or [2], wherein the milliparticles have the median size by weight of between 1 mm and 5 mm.

[4] The tire according to any one of [1] to [3], wherein the milliparticles are hollow milliparticles and/or porous milliparticles.

[5] The tire according to any one of [1] to [4], wherein the milliparticles comprise metal or polymer.

【0010】

[6] The tire according to any one of [1] to [4] wherein the milliparticles comprise metal, metallic oxide, or metallic hydroxide.

[7] The tire according to [6], wherein the metal, the metal of the metallic oxide or the metal of the metallic hydroxide is chosen from the group consisting of aluminum, silicon, zirconium, transition metals and the mixture or alloys thereof.

[8] The tire according to any one of [1] to [4], wherein the milliparticles comprise metallic oxide or metallic hydroxide which is chosen from the group consisting of aluminum oxides and/or hydroxides, silicon oxides or hydroxides, aluminum-silicon oxides or hydroxides, and the mixture thereof.

[9] The tire according to any one of [1] to [4], wherein the milliparticles comprises aluminosilicate.

【0011】

[10] The tire according to any one of [1] to [4], wherein the milliparticles comprising polymer are milliparticles of a thermoplastic polymer or cellulose polymer.

[11] The tire according to any one of [1] to [4], wherein the milliparticles comprise a thermoplastic polymer which is chosen from the group consisting of polystyrene (PS), polyethylene (PE), polypropylene (PP), polyesters, polycarbonate (PC), polyamides (PA) and mixtures thereof.

[12] The tire according to any one of [1] to [11], wherein the diene elastomer is chosen from the group consisting of natural rubber, synthetic polyisoprenes, polybutadienes, butadiene copolymers, isoprene copolymers and the mixtures thereof.

[13] The tire according to [12], wherein the surfacic portion comprises at least 50 phr of natural rubber or of synthetic polyisoprene as the diene elastomer.

【0012】

[14] The tire according to [12] or [13], wherein the surfacic portion comprises at least 50 phr of a polybutadiene having a content of cis-1,4 bonds of greater than 90%.

[15] The tire according to any one of [1] to [14], wherein the reinforcing filler comprises an inorganic filler or a carbon black or a mixture thereof.

[16] The tire according to any one of [1] to [15], wherein the content of total reinforcing filler is between 60 and 120 phr.

[17] The tire according to any one of [1] to [16], wherein the liquid plasticizer is chosen from the group consisting of 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.

[18] The tire according to [17], wherein the content of liquid plasticizer is greater than 40 phr.

【0013】

4. BRIEF DESCRIPTION OF THE DRAWINGS

Other characteristics and advantages of the invention arise from the description made hereafter in reference to the annexed drawings which show, as non-restrictive examples, some embodiments of the object of the invention.

In these drawings:

【0014】

[FIG. 1] FIG. 1 (a) shows a schematic view of a tire cross sectional view according to this invention, and FIG. 1 (b) shows a partial enlarged sectional view of a part indicated by B in FIG. 1 (a);

[FIG. 2] FIG. 2 (a) shows a schematic view of a tire cross sectional view of another variant of this invention, and FIG. 2 (b) shows a partial enlarged sectional view of a part indicated by B in FIG. 2 (a).

【0015】

5. DETAILED DESCRIPTION OF THE INVENTION

The tire (1) of the invention as presented in FIG. 1 and FIG. 2 has a tread (2) having a specific composite structure with a surfacic portion (3) and an internal portion (4), radially adjacent, having a different formulation from the formulation of the surfacic portion (3).

【0016】

The rubber composition composing the surfacic portion (3) of the tread (2) of the tire (1) of the invention comprises at least a diene elastomer, a liquid plasticizer, a reinforcing filler and milliparticles (5), which components are described in detail below.

【0017】

In the present description, unless expressly indicated otherwise, all the percentages (%) shown are % by weight. Moreover, any interval of values denoted by the expression "between a and b" represents the range of values extending from greater than a to less than b (that is to say, limits a and b excluded) whereas any interval of

values denoted by the expression "from a to b" means the range of values extending from a up to b (that is to say, including the strict limits a and b).

【0018】

5-1. Diene elastomer

"Diene" elastomer or rubber should be understood here, in a known manner, as meaning an elastomer resulting at least in part (i.e., a homopolymer or a copolymer) from diene monomers (monomers carrying two carbon-carbon double bonds which may or may not be conjugated).

【0019】

Diene elastomers can be classified in a known way into two categories: those "essentially unsaturated" and those "essentially saturated". Butyl rubbers, such as, for example copolymers of dienes and α-olefins of EPDM type, come within the category of essentially saturated diene elastomers, having a content of units of diene origin which is low or very low, always less than 15% (mol%). In contrast, essentially unsaturated diene elastomer 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%). In the category of "essentially unsaturated" diene elastomers, "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%.

【0020】

It is preferable to use at least one diene elastomer of the highly unsaturated type, in particular a diene elastomer chosen from the group consisting of polybutadienes

(BR), synthetic polyisoprenes (IR), natural rubber (NR), butadiene copolymers, isoprene copolymers and mixtures thereof. Such copolymers are more preferably chosen from the group consisting of butadiene/styrene copolymers (SBR), isoprene/butadiene copolymers (BIR), isoprene/styrene copolymers (SIR), isoprene/butadiene/styrene copolymers (SBIR) and mixtures thereof.

【0021】

The elastomers can, for example, be block, random, sequential or microsequential elastomers and can be prepared in dispersion or in solution; they can be coupled and/or star-branched or also functionalized with a coupling and/or star-branching or functionalization agent. For coupling with carbon black, mention may be made, for example, of functional groups comprising a C-Sn bond or of aminated functional groups, such as benzophenone, for example; for coupling with a reinforcing inorganic filler, such as silica, mention may be made, for example, of silanol functional groups or polysiloxane functional groups having a silanol end (such as described, for example, in US 6 013 718), of alkoxysilane groups (such as described, for example, in US 5 977 238), of carboxyl groups (such as described, for example, in US 6 815 473 or US 2006/0089445) or of polyether groups (such as described, for example, in US 6 503 973). Mention may also be made, as other examples of such functionalized elastomers, of elastomers (such as SBR, BR, NR or IR) of the epoxidized type.

【0022】

The following are preferably suitable: polybutadienes, in particular those having a content of 1,2-units of between 4% and 80% or those having a content of cis-1,4-

units of greater than 80%, polyisoprenes, butadiene/styrene copolymers in particular those having a styrene content of between 5% and 50% by weight and more particularly between 20% and 40%, a content of 1,2-bonds of the butadiene part of between 4% and 65% and a content of trans-1,4-bonds of between 20% and 80%, butadiene/isoprene copolymers, in particular those having an isoprene content of between 5% and 90% by weight and a glass transition temperature ("Tg" - measured according to ASTM D 3418-82) of -40°C to -80°C, or isoprene/styrene copolymers, in particular those having a styrene content of between 5% and 50% by weight and a Tg of between -25°C and -50°C.

【0023】

In the case of butadiene/styrene/isoprene copolymers, those having a styrene content of between 5% and 50% by weight and more particularly of between 10% and 40%, an isoprene content of between 15% and 60% by weight and more particularly between 20% and 50%, a butadiene content of between 5% and 50% by weight and more particularly of between 20% and 40%, a content of 1,2-units of the butadiene part of between 4% and 85%, a content of trans-1,4-units of the butadiene part of between 6% and 80%, a content of 1,2- plus 3,4-units of the isoprene part of between 5% and 70% and a content of trans-1,4-units of the isoprene part of between 10% and 50%, and more generally any butadiene/styrene/isoprene copolymer having a Tg of between -20°C and -70°C, are suitable in particular.

【0024】

According to a particularly preferred embodiment of the invention, the diene elastomer is chosen from the group consisting of natural rubber, synthetic

polyisoprenes, polybutadienes having a content of cis-1,4 bonds of greater than 90%, butadiene/styrene copolymers and the mixtures thereof.

【0025】

According to a more particular and preferred embodiment, the diene elastomer used is predominantly, that is to say for at least 50 phr (The abbreviation "phr" means parts by weight per 100 parts of elastomer), natural rubber (NR) or a synthetic polyisoprene (IR). More preferably, the said natural rubber or synthetic polyisoprene is then used as a blend with a polybutadiene (BR) having a content of cis-1,4 bonds which is preferably greater than 90%.

【0026】

According to another particular and preferred embodiment, the diene elastomer used is predominantly, that is to say for at least 50 phr, a polybutadiene (BR) having a content of cis-1,4 bonds of greater than 90%. More preferably, said polybutadiene is then used as a blend with natural rubber or a synthetic polyisoprene.

【0027】

According to another particular and preferred embodiment, the diene elastomer used is a binary blend (mixture) of NR (or IR) and of BR, or a ternary blend of NR (or IR), BR and SBR. Preferably in the case of such blends, the composition comprises between 25 and 75 phr of NR (or IR) and between 75 and 25 phr of BR, with which may or may not be associated a third elastomer (ternary blend) at a content of less than 30 phr, in particular of less than 20 phr. This third elastomer is preferably an SBR elastomer, in particular a solution SBR ("SSBR"). More preferably still, in the case of such a blend, the composition comprises from 35 to 65 phr of NR (or IR) and

from 65 to 35 phr of BR. The BR used is preferably a BR having a content of cis-1,4 bonds of greater than 90%, more preferably of greater than 95%.

【0028】

Synthetic elastomers other than diene elastomers, indeed even polymers other than elastomers, for example thermoplastic polymers, might be combined, in a minor amount, with the diene elastomers of the compositions of the invention.

【0029】

5-2. Plasticizing system

The rubber composition composing the surfacic portion (3) of the tread (2) of the tire (1) of the invention has as other essential characteristic that of comprising more than 30 phr of a plasticizing agent which is liquid (at 20°C), the role of which is to soften the matrix by diluting the elastomer and the reinforcing filler; its Tg is by definition less than -20°C, preferably less than -40°C.

【0030】

Any extending oil, whether of aromatic or non-aromatic nature, any liquid plasticizing agent known for its plasticizing properties with regard to diene elastomers, can be used. At ambient temperature (20°C), 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 opposed, in particular, to plasticizing hydrocarbon resins which are by nature solid at ambient temperature.

【0031】

Liquid plasticizers chosen from the group consisting of polyolefinic oils, naphthenic oils (low or high viscosity, in particular hydrogenated or otherwise), paraffinic oils, DAE (Distillate Aromatic Extracts) oils, MES (Medium Extracted Solvates) oils, TDAE oils (Treated Distillate Aromatic Extracts), RAE oils (Residual Aromatic Extracts), TRAE oils (Treated Residual Aromatic Extracts), SRAE oils (Safety Residual Aromatic Extracts), mineral oils, vegetable oils, ether plasticizers, ester plasticizers, phosphate plasticizers, sulphonate plasticizers and the mixtures thereof are particularly suitable.

【0032】

Mention may be made, as phosphate plasticizers for example, of those that contain between 12 and 30 carbon atoms, for example trioctyl phosphate. As examples of ester plasticizers, mention may especially be made of the compounds chosen from the group consisting of trimellitates, pyromellitates, phthalates, 1,2-cyclohexane dicarboxylates, adipates, azelates, sebacates, triesters of glycerol, and mixtures thereof. Among the above triesters, mention may be made of glycerol triesters, preferably composed predominantly (for more than 50% by weight, more preferably for more than 80% by weight) of an unsaturated C_{18} fatty acid, that is to say an unsaturated fatty acid chosen from the group consisting of oleic acid, linoleic acid, linolenic acid and the mixtures thereof. More preferably, whether of synthetic origin or natural origin (in the case, for example, of sunflower or rapeseed vegetable oils), the fatty acid used is composed for more than 50% by weight, more preferably still from 80% by weight, of oleic acid. Such triesters (trioleates) comprising a high

content of oleic acid are well known; for example they have been described in Application WO 02/088238, as plasticizing agents in treads for tires.

【0033】

The content of liquid plasticizer in the composition of the invention is preferably greater than 40 phr, more preferably included within a range from 50 to 100 phr.

【0034】

According to another preferred embodiment, the compositions of the invention can also comprise, as plasticizer which is solid (at 20°C), a hydrocarbon resin exhibiting a Tg of greater than +20°C, preferably greater than +30°C, such as is described, for example in Applications WO 2005/087859, WO 2006/061064 and WO 2007/017060.

【0035】

Hydrocarbon resins are polymers well known to a person skilled in the art which are essentially based on carbon and hydrogen and thus miscible by nature in diene elastomer composition(s), when they are additionally described as being "plasticizing". They have been described, for example, in the work entitled "*Hydrocarbon Resins*" by R. Mildenberg, M. Zander and G. Collin (New York, VCH, 1997, ISBN 3-527-28617-9), chapter 5 of which is devoted to their applications, in particular in the tire rubber field (5.5. "*Rubber Tires and Mechanical Goods*"). 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 oil-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.

【0036】

Preferably, the plasticizing hydrocarbon resin exhibits at least one, more preferably all, of the following characteristics:

- a Tg of greater than 20°C (more preferably between 40 and 100°C);
- a number-average molecular weight (Mn) of between 400 and 2000 g/mol (more preferably between 500 and 1500g/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).

【0037】

The Tg is measured in a known way by DSC (*Differential Scanning Calorimetry*) according to Standard ASTM D3418 (1999). The macrostructure (Mw, Mn and PI) of the hydrocarbon resin 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").

【0038】

According to a particularly preferred embodiment, the plasticizing hydrocarbon resin is chosen 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 and the mixtures thereof. Use is more preferably made, among the above copolymer resins, of those chosen 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/vinylaromatic copolymer resins, C_9 fraction/vinylaromatic copolymer resins, and the mixtures thereof.

【0039】

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.

【0040】

The content of hydrocarbon resin is preferably between 3 and 60 phr, more preferably between 3 and 40 phr, in particular between 5 and 30 phr.

【0041】

The content of total plasticizing agent (i.e., liquid plasticizer plus, if appropriate, solid hydrocarbon resin) is preferably between 40 and 100 phr, more preferably included within a range of from 50 to 80 phr.

【0042】

5-3. Reinforcing filler

Use may be made of any type of reinforcing filler known for its capabilities of reinforcing a rubber composition which can be used for the manufacture of tires, for example an organic reinforcing filler, such as carbon black, or a reinforcing inorganic filler, such as silica, with which a coupling agent is combined in a known way.

【0043】

Such a reinforcing filler typically consists of nanoparticles, the mean size (by weight) (see, for example, ISO-13320 (Particle size analysis-Laser diffraction methods), of which is less than 500 nm, generally between 20 and 200 nm, in particular and preferably between 20 and 150 nm.

【0044】

All carbon blacks, in particular blacks of the HAF, ISAF or SAF type, conventionally used in treads for tires ("tire-grade" blacks) are suitable as carbon blacks. Mention will more particularly be made, among the latter, of the reinforcing carbon blacks of the 100, 200 or 300 series (ASTM grades), such as, for example, the

N115, N134, N234, N326, N330, N339, N347 or N375 blacks. The carbon blacks might, for example, be already incorporated in the isoprene elastomer in the form of a masterbatch (see, for example, Applications WO 97/36724 or WO 99/16600).

【0045】

Mention may be made, as examples of organic fillers other than carbon blacks, of the functionalized polyvinyl organic fillers as described in Applications WO 2006/069792, WO 2006/069793, WO2008/003434 and WO2008/003435.

【0046】

The term "reinforcing inorganic filler" should be understood here as meaning any inorganic or mineral filler, whatever its colour and its origin (natural or synthetic), also known as "white filler" or sometimes "clear filler" in contrast to carbon black, capable of reinforcing by itself, 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 way, by the presence of hydroxyl (-OH) groups at its surface.

【0047】

Mineral fillers of the siliceous type, in particular silica (SiO_2), or of the aluminous type, in particular alumina (Al_2O_3), are suitable in particular as reinforcing inorganic fillers. The silica used can be any reinforcing silica known to a person skilled in the art, in particular any precipitated or pyrogenic silica exhibiting a BET surface and a CTAB specific surface both of less than 450 m^2/g, preferably from 30 to 400 m^2/g, in particular between 60 and 300 m^2/g. Mention will be made, as highly dispersible

("HD precipitated silicas"), for example, of the Ultrasil 7000 and Ultrasil 7005 silicas from Evonik, the "Zeosil" 1165MP, 1135MP and 1115MP silicas from Rhodia, the "Hi-Sil" EZ150G silica from PPG, the "Zeopol" 8715, 8745 and 8755 silicas from Huber. Mention may be made, as examples of reinforcing aluminas, of the "Baikalox A125" or "Baikalox CR125" aluminas from Baïkowski, the "APA-100RDX" alumina from Condea, the "Aluminoxid C" alumina from Degussa or the "AKP-G015" alumina from Sumitomo Chemicals.

【0048】

Preferably, the content of total reinforcing filler (carbon black and/or reinforcing inorganic filler) is between 60 and 120 phr, in particular between 70 and 100 phr.

【0049】

According to a specific embodiment, the reinforcing filler comprises predominantly carbon black; in such a case, the carbon black is present at a content preferably of greater than 60 phr, in combination or not with a reinforcing inorganic filler, such as silica, in a minor amount.

【0050】

According to another specific embodiment, the reinforcing filler comprises predominantly an inorganic filler, in particular silica; in such a case, the inorganic filler, in particular silica, is present at a content preferably of greater than 70 phr, in combination or not with carbon black in a minor amount; the carbon black, when it is present, is preferably used at a content of less than 20 phr, more preferably less than 10 phr (for example between 0.1 and 10 phr).

【0051】

Independently of the first aspect of the invention, namely the search for optimized grip on snow and ice, the predominant use of a reinforcing inorganic filler, such as silica, is also advantageous from the viewpoint of the grip on a wet ground surface.

【0052】

According to another possible embodiment of the invention, the reinforcing filler comprises a blend of carbon black and of reinforcing inorganic filler such as silica, in similar amounts; in such a case, the content of inorganic filler, in particular silica, and the content of carbon black are preferably each between 25 and 75 phr, more particularly each between 30 and 50 phr.

【0053】

In order to couple the reinforcing inorganic filler to the diene elastomer, use is made, in a well-known way, of an at least bifunctional coupling agent (or bonding agent) intended to provide a satisfactory connection, of chemical and/or physical nature, between the inorganic filler (surface of its particles) and the diene elastomer. Use is made, in particular, of bifunctional organosilanes or polyorganosiloxanes.

【0054】

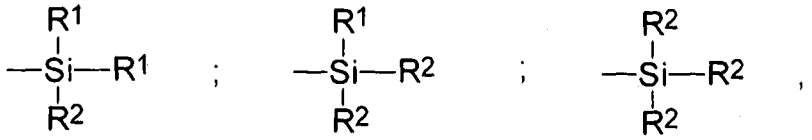
Use is made in particular of silane polysulphides, referred to as "symmetrical" or "asymmetrical" depending on their specific structure, as described, for example, in Applications WO 03/002648 (or US 2005/016651) and WO 03/002649 (or US 2005/016650).

【0055】

"Symmetrical" silane polysulphides corresponding 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, 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:



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 chosen from C_1-C_8 alkoxyls and C_5-C_8 cycloalkoxyls, more preferably still a group chosen from C_1-C_4 alkoxyls, in particular methoxyl and ethoxyl),

are suitable in particular, without the above definition being limiting.

【0056】

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(triethoxysilylpropyl) disulphide, abbreviated to TESPD, of formula $[(C_2H_5O)_3Si(CH_2)_3S]_2$. 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).

【0057】

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.

【0058】

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 or WO 2007/098080.

【0059】

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

【0060】

In the rubber compositions in accordance with the invention, the content of coupling agent is preferably between 2 and 15 phr, more preferably between 3 and 12 phr.

【0061】

A person skilled in the art will understand that a reinforcing filler of another nature, in particular organic nature, 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.

【0062】

The rubber composition composing the internal portion (4) of the tread (2) of the tire (1) of the invention also comprises the diene elastomer, the plasticizing agent and the reinforcing filler such as those present in the surfacic portion (3).

【0063】

5-4. Milliparticles

The rubber composition composing the surfacic portion (3) of the tread (2) of the tire (1) of the invention has the essential characteristic of comprising milliparticles (5) having a median size (distribution by weight) of more than 1 mm in a volume fraction of the milliparticles of more than 20% in volume of the rubber composition of the surfacic portion (3).

【0064】

By "milliparticles" or "millimetric particles" (both terms being synonymous) is understood to mean, by definition, particles of millimetric size, that is to say for which the median size (expressed by weight) is between 1 mm and 1cm.

【0065】

Similarly, "millicavities" or "millimetric cavities" mean cavities of millimetric size, and "milliroughness" or "millimetric roughness" means roughness of millimetric size.

【0066】

Preferably, these milliparticles have a median size by weight of between 1 mm and 5 mm. Below the minimum indicated above, the targeted technical effect (namely the creation of a suitable milliroughness) is inadequate and so that the milliparticles have a median size by weight of more preferably 1.2 mm or more, still more preferably 1.5 mm or more.

Whereas, above the maximum indicated, various disadvantages emerge, in particular when the rubber composition is used as tread: apart from a possible aesthetic loss and

a risk of cohesion loss during rolling of relatively large elements of the tread pattern, it being found that the grip performance on snow and/or ice may be damaged.

【0067】

For all these reasons, it is preferable for the milliparticles to have a median size of between 1 mm and 4 mm, more preferably between 1 mm and 3 mm. This particularly preferred size range appears to correspond to an optimized compromise between, on the one hand, a desired surface roughness and, on the other hand, good contact between the rubber composition and snow/ice.

【0068】

Moreover, for identical reasons to those set out above, the volume fraction is preferably more than 30% (notably between 30% and 70%), more preferably more than 40% (notably between 40% and 65%), still more preferably between 40% and 60% in volume of the rubber composition of the surfacic portion (3).

【0069】

The volume fraction as used in the field of this invention is the ratio of the volume of the milliparticles to the volume of the rubber composition (total volume, including the milliparticles) composing the surfacic portion (3) of the tread (2) of the invention.

【0070】

The equation formula for the ratio can be described as follow.

$V_f = V_P / V_{PR}$

Wherein:

V_f: Volume fraction of the milliparticles in volume of the rubber composition of the surfacic portion (3)

V_P: Volume of the milliparticles in the rubber composition of the surfacic portion (3)

V_{PR}: Volume of the rubber composition (total volume, including the milliparticles) of surfacic portion (3)

【0071】

In addition, the equation formula can be also mentioned below.

$V_f=(Q_P/D_P)/(Q_P/D_P+Q_R/D_R)$

Wherein:

Q_P: Content of the milliparticles composing the rubber composition of the surfacic portion (3) (phr)

Q_R: Content of the rubber composition of the surfacic portion (3) excluding the milliparticles (phr)

D_P: Specific gravity (density) of the milliparticles composing and extracted from the rubber composition of the surfacic portion (3) (g/cm^3)

D_R: Specific gravity (density) of the rubber composition of the surfacic portion (3) excluding the milliparticles (g/cm^3)

【0072】

Various known methods are applicable for the analysis of the above specific gravity (density). For example, immersion method, liquid pycnometer method and titration method (see, for example Standard ISO1183, ASTM D792).

【0073】

The invention applies to all types of milliparticles, whether the milliparticles are solid, for instance porous or not, or hollow or not, for instance in the form of a

powder or in any other form (for instance, spherical, cubic, pyramidal, conic, parallelepiped, ovoid or even random).

【0074】

According to a preferred embodiment, the milliparticles are hollow milliparticles. In this configuration such hollow milliparticles are able to create extra cavities which scrape snow on ground and which makes possible to improve grip on snow. Moreover, the extra cavities act as storage volume and as channel for draining the water or the water film layer on snow or ice surface after crushing by breaking a hollow structure, even without expulsion from the rubber matrix, thus the friction coefficient at tire new state is further improved.

【0075】

According to another preferred embodiment, the milliparticles are porous milliparticles. Pores of porous milliparticles are able to absorb water and to drain effectively the water or the water film layer on a snowy or icy road surface even without expulsion from the rubber matrix; thus the friction coefficient at tire new state is further improved. Furthermore, an edge of wall of the pore and the porous milliparticles after crushing by breaking a porous structure may generate claw effect on snow and ice surfaces.

【0076】

According to another preferred embodiment, the milliparticles are milliparticles of metal or polymer.

【0077】

According to a more preferred embodiment, the milliparticles comprising metal are milliparticles of metal, metallic oxide, metallic hydroxide or metal salt.

【0078】

According to a still more preferred embodiment, the metal, the metal of the metallic oxide or the metal of metallic hydroxide is chosen from the group consisting of aluminum, silicon, zirconium, transition metals and the mixtures or alloys thereof. Transition metal is understood to mean more particularly the metals from the fourth period ranging from scandium to zinc, preferably titanium and zinc. More preferably still, aluminum, silicon, titanium, zirconium and zinc are suitable.

【0079】

According to a still more preferred embodiment, the metallic oxide or the metallic hydroxide is chosen from the group consisting of aluminum oxides and/or hydroxides, silicon oxides and/or hydroxides, aluminum-silicon oxides and/or hydroxides, and the mixtures thereof. More preferably still, the metallic oxide used is an aluminosilicate.

【0080】

According to a still more preferred embodiment, the salt of the metal salt is chosen from the group consisting of chloride, carbonate, sulphate and the mixture thereof, and the metal of the metal salt is an alkali metal or an alkaline earth metal. More preferably still, the alkali metal or the alkaline earth metal is chosen from the group consisting of Na, K, Ca, Mg and the mixture thereof.

【0081】

According to a more preferred embodiment, the milliparticles comprising polymer are milliparticles of thermoplastic polymer or cellulose polymer.

【0082】

According to a still more preferred embodiment, the thermoplastic polymer is chosen from the group consisting of polystyrene (PS), polyethylene (PE), polypropylene (PP), polyesters (for example: polyethylene terephthalate (PET)), polycarbonate (PC), polyamides (PA) and mixtures thereof.

【0083】

Various known methods are applicable for the analysis of the distribution of the particle size and the calculation of the median size of the milliparticles (or median diameter for milliparticles assumed to be substantially spherical), for example by laser diffraction (see, for example Standard ISO 8130 13 or Standard JIS K5600-9-3).

【0084】

Use may also simply and preferably be made of an analysis of the milliparticles size distribution by mechanical sieving; the operation consists of sieving a defined amount of sample (for example 200 g) on a vibrating table for 30 min with different sieve diameters (for example, according to a progressive ratio equal to 1.26, with meshes for instance from about 6 mm to about 50 μm depending on the size of the specific particles to be analyzed); the oversize collected in each sieve is weighed on a precision balance; the % of oversize for each mesh diameter with respect to the total weight of product is deduced therefrom; the median size (or median diameter) or mean size (or mean diameter) is finally calculated in a known way from the histogram of the particle size distribution.

【0085】

The rubber composition composing the internal portion (4) of the tread (2) of the tire (1) of the invention is made of the rubber composition which is different from the rubber composition of the surfacic portion (3).

【0086】

According to a preferred embodiment, the rubber composition composing the internal portion (4) is devoid of milliparticles or contains milliparticles (6), and a volume fraction of the milliparticles (6) in volume of the rubber composition of the internal portion (4) is lower than the volume fraction of the milliparticles (5) in volume of the rubber composition of the surfacic portion (3), preferably is totally devoid of the milliparticles (6).

【0087】

The volume fraction of the milliparticles (6) in volume of the rubber composition of the internal portion (4) is the ratio of the volume of the milliparticles to the volume of the rubber composition (total volume, including the milliparticles) composing the internal portion (4) of the tread (2) of the invention such as those present in the surfacic portion (3).

【0088】

5-5. Various additives

The rubber compositions may also comprise all or a portion of the usual additives generally used in the elastomer compositions intended for the manufacture of treads for tires, in particular for winter tires, such as, for example, protection agents, such as antiozone waxes, chemical antiozonants, antioxidants, reinforcing resins, methylene

acceptors (for example phenolic novolac resin) or methylene donors (for example HMT or H3M), a crosslinking system based either on sulphur or on donors of sulphur and/or peroxide and/or bismaleimides, vulcanization accelerators, or vulcanization activators.

【0089】

These compositions can also comprise coupling activators when a coupling agent is used, agents for covering the 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.

【0090】

FIG. 1. shows a schematic view of a tire cross sectional view of a pneumatic tire tread (2) of dimension 205/55R16, such tread (2) being provided with two portions, firstly a surfacic portion (3) composing part of a contact face intended to come into contact with ground during rolling at least when such tread (2) is new, and secondly an internal portion (4) made of a rubber composition with a formulation different from the formulation of the rubber composition composing the surfacic portion (3), and adjacent to the surfacic portion (3). The internal construction of this pneumatic tire (1) other than the tread (2), is the same structure as conventional pneumatic radial tire, thus description of the internal construction will be omitted.

【0091】

The thickness (measured in the radial direction of the tire) of the surfacic portion (3) is more than 1 mm. Below the minimum indicated above, it may be difficult to contain and/or hold the milliparticles in the surfacic portion (3) at new state of the tread of the pneumatic tire. This thickness is preferably between 1 mm and 5 mm, more preferably between 1 mm and 4 mm, and still more preferably between 1 mm and 3 mm in order to effectively improve grip on snow and ice especially at new state and/or initial using time of the tread of the pneumatic tire by the milliparticles (5) which have the median size by weight of more than 1 mm (preferably between 1 mm and 4 mm, more preferably between 1 mm and 3 mm) and efficiently appear on a rolling surface intended to come into contact with a ground surface during running of the pneumatic. Most preferably, this thickness is from 1.5 mm to 2 mm.

【0092】

The surfacic portion (3) comprises the milliparticles (5) having the volume fraction more than 20% in volume of the rubber composition of the surfacic portion (3), the milliparticles (5) are partly exposed without being totally or partly covered by a rubber skin, which results creating roughness on the tire rolling surface in the new state. Then after such surfacic portion (3) wears out and the internal portion (4) starts touching with ground during rolling which already has roughness on its contact face.

【0093】

Preferably, the thickness (measured in the radial direction of the tire) of the internal portion (4) adjacent to the surfacic portion (3) is more than 1 mm, more preferably more than 2 mm, still more preferably more than 3 mm, notably between 6 mm and 9 mm. Most preferably, this thickness is from 8 mm to 8.5 mm.

【0094】

More preferably, the rubber composition composing the internal portion (4) of the tread (2) is totally devoid of milliparticles or contains milliparticles in a volume fraction of less than 10%, still more preferably less than 5%, particularly less than 2% in volume of the rubber composition of the internal portion (4), more particularly is totally devoid of such milliparticles in order to avoid a risk of cohesion loss during rolling of relatively large elements of the tread pattern because the internal portion (4) starts touching with ground during rolling which has roughness on its contact face after the surfacic portion (3) wears out. Such milliparticles (5, 6) can be of the same kind for both the surfacic portion (3) and (if present) the internal portion (4), or can be different kinds between the surfacic portion (3) and (if present) the internal portion (4). The surfacic portion (3) and/or the internal portion (4) can be made of a non-foamed rubber composition.

【0095】

According to another preferred embodiment, the rubber composition composing the internal portion (4) is a foamed rubber composition devoid or having predetermined content of milliparticles and/or microparticles in order to maintain improvement of friction coefficient on snow and ice provided by the surfacic portion (3) after wearing the surfacic portion (3). Preferably, the internal portion (4) is made of the foamed rubber composition which is totally devoid of such milliparticles.

【0096】

The surfacic portion (3) can be made, either all over the tread (2) including a part not contacting with ground, or only on the part of the tread (2) contacting with ground during rolling, as shown in figure 2.

【0097】

FIG. 2. shows a variant of this invention. In this figure 2 also, the tread (2) being provided with two portions, the surfacic portion (3) composing part of the contact face intended to come into contact with ground during rolling at least when such tread (2) is new, and the internal portion (4) made of a rubber composition different with the rubber composition composing the surfacic portion (3) and adjacent to the surfacic portion (3). The surfacic portion (3) in this figure is formed only on the part of the tread (2) which contacts really with ground.

【0098】

The advantage of this configuration is to be able to precisely placing the surfacic portion (3) where such surfacic portion (3) is really useful, thus efficiency to have such surfacic portion (3) for improving grip on snow and ice at new state is increased.

【0099】

According to a preferred embodiment, the rubber composition composing the internal portion (4) is devoid or contains less than 2% (in volume of the rubber composition of the internal portion (4)) of milliparticles (6) such as that in the surfacic portion (3), preferably is totally devoid of the milliparticles (6).

【0100】

According to another preferred embodiment, the rubber composition composing the internal portion (4) is a foamed rubber composition. The internal portion (4) is made

of the foamed rubber composition which is devoid orcontains less than 2% (in volume of the rubber composition of the internal portion (4)) of the milliparticles (6) such as that in the surfacic portion (3)), preferably is totally devoid of the milliparticles (6). Such milliparticles (5, 6) can be of the same kind for both the surfacic portion (3) and (if present) the internal portion (4), or can be different kinds between the surfacic portion (3) and (if present) the internal portion (4). The surfacic portion (3) and/or the internal portion (4) can be made of a non-foamed rubber composition.

【0101】

5-6. Manufacture of the rubber compositions and of the treads

The rubber compositions composing the surfacic and the internal portions (3, 4) of the tread (2) of the invention are manufactured in appropriate mixers using two successive preparation phases according to a general procedure well known to a person skilled in the art: a first phase of thermomechanical working or kneading (sometimes described as "non-productive" phase) at high temperature, up to a maximum temperature of between 130°C and 200°C, preferably between 145°C and 185°C, followed by a second phase of mechanical working (sometimes described as "productive" phase) at a lower temperature, typically of less than 120°C, for example between 60°C and 100°C, finishing phase during which the crosslinking or vulcanization system is incorporated.

【0102】

A process which can be used for the manufacture of such compositions forming the surfacic portion (3) of the treads (2) according to the invention comprises, for example and preferably, the following steps:

- incorporating in the diene elastomer, in a mixer, more than 30 phr of a liquid plasticizer, within a range from 50 to 150 phr of a reinforcing filler, milliparticles having a median size by weight of more than 1 mm and the milliparticles having predetermined content making a volume fraction of the milliparticles more than 20% in volume of the rubber composition of the surfacic portion (3), everything being kneaded thermomechanically, in one or more goes, until a maximum temperature of between 130°C and 200°C is reached;
- cooling the combined mixture to a temperature of less than 100°C;
- subsequently incorporating a crosslinking system;
- kneading everything up to a maximum temperature of less than 120°C;
- extruding or calendering the rubber composition thus obtained, in particular in the form of a surfacic portion (3) of a tire tread (2).

【0103】

By way of example, the first (non-productive) phase is carried out in a single thermomechanical stage during which all the necessary constituents, the optional additional covering agents or processing aids, and various other additives, with the exception of the crosslinking system, are introduced into an appropriate mixer, such as a normal internal mixer. After cooling the mixture thus obtained during the first non-productive phase, the crosslinking system is then incorporated at low

temperature, generally in an external mixer, such as an open mill; everything is then mixed (productive phase) for a few minutes, for example between 5 and 15 min.

【0104】

The crosslinking system proper 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 3.0 phr, and that of the primary accelerator is preferably between 0.5 and 5.0 phr.

【0105】

Use may be made, as accelerator (primary or secondary) of any compound capable of acting as accelerator of the vulcanization of diene elastomers in the presence of sulphur, in particular accelerators of the thiazoles type and their derivatives, accelerators of thiurams types, or zinc dithiocarbamates. These accelerators are more preferably chosen from the group consisting of 2-mercaptobenzothiazyl disulphide (abbreviated to "MBTS"), N-cyclohexyl-2-benzothiazolesulphenamide (abbreviated to "CBS"), N,N-dicyclohexyl-2-benzothiazolesulphenamide ("DCBS"), N-tert-butyl-2-benzothiazolesulphenamide ("TBBS"), N-tert-butyl-2- benzothiazolesulphenimide ("TBSI"), zinc dibenzyldithiocarbamate ("ZBEC"), Tetrabenzylthiuram disulfide ("TBZTD") and the mixtures thereof.

【0106】

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 a part of a winter tire tread.

【0107】

As for making a pneumatic tire (1) according to the invention, one can also build a first layer of a homogeneous rubber composition having a concentration in milliparticles having a median size by weight of more than 1 mm and a volume fraction of the milliparticles more than 20% (in volume of the rubber composition) and a second layer devoid of milliparticles or having a lower concentration than the first layer, then superpose the first layer onto the second layer to get a raw tread band, and then build and mold a tire. The first layer forming the surfacic portion (3) is located so as to contact the road in the new state of the tire.

【0108】

The vulcanization (or curing) is carried out in a known way at a temperature generally of between 130°C and 200°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.

【0109】

The invention relates to the tires described above, both in the raw state (i.e., before curing) and in the cured state (i.e., after crosslinking or vulcanization).

【0110】

6. EXAMPLES OF THE IMPLEMENTATION OF THE INVENTION

6-1. Preparation of the rubber compositions composing the surfacic portion and of the treads

In the following tests, four compositions (identified as C-1, C-2, C-3 and C-4) based on diene elastomers (NR and BR blend), are compared, which compositions are reinforced with a blend of silica and carbon black with which is combined a fraction of milliparticles comprising porous cellulose beads or sodium chloride, or is combined a fraction of microparticles comprising sodium chloride, or is not combined either as follows:

- composition C-1: control composition (without milliparticles/microparticles);
- composition C-2: composition in accordance with the invention, with 200 phr of porous cellulose beads milliparticles (median size of around 2 mm);
- composition C-3: composition in accordance with the invention, with 500 phr of sodium chloride milliparticles (median size of around 1.5 mm);
- composition C-4: composition with 500 phr of sodium chloride microparticles (median size of around 200 μm).

【0111】

All the median sizes (weight distribution) indicated above are measured by mechanical sieving as indicated in paragraph 5-4 above. The compositions C-2 and C-3 comprising milliparticles are therefore in accordance with the invention.

【0112】

The formulations of the four compositions (Table 1 – contents of the various products expressed in phr) are given in Table 1; the vulcanization system is

composed of sulphur and sulphenamide. The reinforcing filler (in this example silica as reinforcing inorganic filler, its associated coupling agent, and small amount of carbon black), the plasticizer, each of milliparticles or microparticles, the diene elastomer (or blend of diene elastomers) and the various other ingredients, 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 lasted in total approximately 3 to 4 minutes, until a maximum "dropping" temperature of 165°C wasreached. 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 30°C, everything being mixed (productive phase) for an appropriate time (for example between 5 and 12 min). Each compositions thus obtained were subsequently calendered, either in the form of plaques (thickness of 2 to 3 mm) or of fine sheets of rubber for the following tests.

【0113】

Each specific gravity (density) of the milliparticles or the microparticles composing and extracted from C-2, C-3 and C-4 and the corresponding compositions excluding the milliparticles or the microparticles, is measured by immersion method as indicated in the paragraph 5-4 above. Each volume fraction is calculated from each specific gravity (density) as indicated in the paragraph 5-4 above (the microparticles instead of milliparticles in case of the composition C-4). Each specific gravity (density) and volume fractions of the compositions are given in Table 2.

【0114】

6-2. Friction test (snow test) on rubber block

These four compositions were subjected to a laboratory test consisting in measuring their friction coefficient on snow. The principle is based on a block of a rubber composition that slides at a given speed (for example equal to 5 km/h) over a snow track with an imposed load (for example equal to 3 kg/cm^2). The forces generated in the direction of travel (Fx) of the block and perpendicular to the travel (Fz) are measured. The Fx/Fz ratio determines the friction coefficient of the test specimen on the snow. The snow temperature was set at -10°C, and the snow test was conducted on a hard pack snow track with a CTI penetrometer reading of around 90 in according to Standard ASTM F1805. The milliparticles or the microparticles had been extracted from the surfaces of blocks by mechanical abrasion treatment which had been reproducing tire rolling condition at beginning of usage. This treatment had been done for the compositions C-2, C-3 and C-4 before the friction test on snow in order to expose the millicavities or the microcavities on the surface.

【0115】

This test, the principle of which is well known to a person skilled in the art (see, for example, patent applications EP 1 052 270 and EP 1 505 112) makes it possible to evaluate, under representative conditions, the grip on ice/snow which would be obtained after a running test on a vehicle fitted with tires whose tread is composed of the same rubber compositions.

【0116】

The results are expressed in Table 3. A value above that of the control (composition C-1), arbitrarily set at 100, indicates an improved result, that is to say an aptitude for shorter braking distance. It is observed in this Table 3 that the compositions C-2 and C-3 in accordance with the invention have a definite increase (5 ~ 6%) in the friction coefficient on the snow, relative to the control composition C-1. The other composition C-4, which is not in accordance with the invention, does not show any improvement of the snow friction coefficient relative to the control composition C-1.

【0117】

6-3. Tests on tires

In order to further confirm the effect of the present invention, the rubber compositions C-1 and C-2 tested above have been used in the treads of control tires (denoted T-1) and tires in accordance with the invention (denoted T-2), as follows:

- composition C-1 forming the whole tread (thickness 10 mm) of the control tires T-1, and also the internal portion (thickness 8.5 mm) of the tires of the invention T-2;
- composition C-2 forming exclusively the surfacic portion (thickness 1.5 mm) of the tires T-2 of the invention. (The milliparticles were partly exposed without being totally covered by the rubber skin.)

These tires, for radial carcass passenger vehicle winter tires, having a size of 205/55R16, were conventionally manufactured and in all respects identical apart from the rubber compositions forming their surfacic portions of treads. Each rubber composition forming their internal portions of treads of these tires was devoid of each of milliparticles.

【0118】

All the tires were fitted to the front and rear a motor vehicle, under nominal tire inflation pressure, and were first of all subjected to rolling on a circuit [of 50km (T-1), 100 km (T-2)], on a dry ground surface for running in and the beginning of wear.

【0119】

A 1,400 cc passenger car provided on all the four wheels with the same kind of test tires under 220 kPa of tire inflation pressure mounted onto 6.5Jx16 rim was run on a snow covered road at a temperature of -12°C, the acceleration from 10 to 25 km/h with 1st gear during acceleration at full throttle under the control of the activated TCS system was measured, and the deceleration from 50 to 5 km/h during sudden longitudinal braking while anti-lock braking system (ABS) activated was measured. The above snow tests were conducted on a hard pack snow with a CTI penetrometer reading of 87 in according to Standard ASTM F1805.

【0120】

Moreover, the above passenger car with the above test tires under the above tire inflation pressure mounted onto the above rim was run on an ice covered road at a temperature of -2°C, and the braking distance from 20 to 5 km/h during sudden longitudinal braking while anti-lock braking system (ABS) activated was measured.

【0121】

The results of the running tests on snow and ice roads are reported in Table 4, in relative units, the base 100 being selected for the control tire T-1 (it should be remembered that a value of greater than 100 indicates an improved performance).

【0122】

It is noted in this Table 4 that the improvement of the grip performances (acceleration on snow and braking on snow/ice) of the tires of the invention (T-2 tires) is very substantially increased in comparison to the control tire results (T-1 tires).

【0123】

In conclusion, the tread in accordance with the invention comprising milliparticles in its surfacic portion, gives the tires a combined braking and acceleration performances on snow/ice that are significantly improved.

【0124】

Table 1

Rubber Composition No.:	C-1	C-2	C-3	C-4
BR (1)	60	60	60	60
NR (2)	40	40	40	40
Silica (3)	80	80	80	80
Coupling agent (4)	6.4	6.4	6.4	6.4
Milliparticles (5)	-	200	-	-
Milliparticles (6)	-	-	500	-
Microparticles (7)	-	-	-	500
Carbon black (8)	5	5	5	5
Non aromatic oil (9)	50	50	50	50
Hydrocarbon resin (10)	10	10	10	10
DPG (11)	1.9	1.9	1.9	1.9
ZnO	1.3	1.3	1.3	1.3
Stearic acid	1	1	1	1
Antiozone wax	1.5	1.5	1.5	1.5
Antioxidant (12)	2	2	2	2
Sulphur	2	2	2	2
Accelerator (13)	1.7	1.7	1.7	1.7

(1) BR with 0.3% of 1,2-; 2.7% of trans; 97% of cis-1,4- (Tg = -104°C);

(2) Natural rubber (peptised);

(3) Silica "Zeosil 1165MP" from Rhodia

(4) Coupling agent TESPT ("Si69" from Degussa);

(5) Porous cellulose beads (Viscopearl-A Series from RENGO CO., LTD), (median size of the particles: around 2 mm);

(6) Sodium chloride ("Minaminokiwami" from Cheetham Salt), (median size of the particles: around 1.5 mm);

(7) Sodium chloride ("Minaminokiwami" from Cheetham Salt), (median size of the particles: around 200 μm);

(8) Grade ASTM N234 (Cabot);

(9) MES oil ("Catenex SNR" from Shell)

(10) Escorez 2173 Resin (Exxon)

(11) Diphenylguanidine (Perkacit DPG from Flexsys);

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

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

Table 2

Rubber composition No.:	C-2	C-3	C-4
Specific gravity of milliparticles or microparticles composing each composition (g/cm^3)	0.86	2.17	2.17
Specific gravity of each composition excluding milliparticles or microparticles (g/cm^3)	1.14	1.14	1.14
Volume fraction (%)	49%	49%	49%

Table 3

Rubber composition No.:	C-1	C-2	C-3	C-4
Friction on snow (-10°C)[*1]	100	105	106	96

(1) Sliding speed: 0.5m/s

Table 4

Tire No.:	T-1	T-2
Acceleration on snow (-12°C)	100	116
Braking on snow (-12°C)	100	109
Braking on ice (-2°C)	100	130

【0125】

7. REFERENCE SIGNS LIST

1. Pneumatic tire
2. Tread of the pneumatic tire
3. Surfacic portion
4. Internal portion
5. Milliparticles in the surfacic portion
6. Milliparticles in the internal portion

CLAIMS

1. A pneumatic tire having a tread comprising at least two radially superposed portions comprising:

- a surfacic portion intended to come into contact with ground during rolling at least when the tread is new and in the cured state, having a thickness of more than 1 mm and being made of a rubber composition,

- an internal portion adjacent to the surfacic portion, having a thickness of more than 1 mm and being made of a rubber composition which is different from the rubber composition of the surfacic portion,

wherein the rubber composition of the surfacic portion comprises at least:

- a diene elastomer;
- more than 30 phr of a liquid plasticizer;
- 50 to 150 phr of a reinforcing filler; and
- milliparticles having a median size by weight of more than 1 mm, in a volume fraction of the milliparticles of more than 20% in volume of the rubber composition of the surfacic portion.

2. The tire according to Claim 1, wherein the volume fraction of the milliparticles is more than 30% in volume of the rubber composition of the surfacic portion.

3. The tire according to Claim 1 or Claim 2, wherein the milliparticles have the median size by weight of between 1 mm and 5 mm.

4. The tire according to any one of Claims 1 to 3, wherein the milliparticles are hollow milliparticles and/or porous milliparticles.

5. The tire according to any one of Claims 1 to 4, wherein the milliparticles comprise metal or polymer.

6. The tire according to any one of Claims 1 to 4, wherein the milliparticles comprise metal, metallic oxide or metallic hydroxide.

7. The tire according to Claim 6, wherein the metal, the metal of the metallic oxide or the metal of the metallic hydroxide is chosen from the group consisting of aluminum, silicon, zirconium, transition metals and the mixture or alloys thereof.

8. The tire according to any one of Claims 1 to 4, wherein the milliparticles comprise metallic oxide or the metallic hydroxide which is chosen from the group consisting of aluminum oxides and/or hydroxides, silicon oxides or hydroxides, aluminum-silicon oxides or hydroxides, and the mixture thereof.

9. The tire according to any one of Claims 1 to 4, wherein the milliparticles comprise aluminosilicate.

10. The tire according to any one of Claims 1 to 4, wherein the milliparticles comprise a thermoplastic polymer or cellulose polymer.

11. The tire according to any one of Claim 1 to 4, wherein the milliparticles comprise a thermoplastic polymer which is chosen from the group consisting of polystyrene (PS), polyethylene (PE), polypropylene (PP), polyesters, polycarbonate (PC), polyamides (PA) and mixtures thereof.

12. The tire according to any one of Claims 1 to 11, wherein the diene elastomer is chosen from the group consisting of natural rubber, synthetic polyisoprenes, polybutadienes, butadiene copolymers, isoprene copolymers and the mixtures thereof.

13. The tire according to Claim 12, wherein the surfacic portion comprises at least 50 phr of natural rubber or of synthetic polyisoprene as the diene elastomer.

14. The tire according to Claim 12 or Claim 13, wherein the surfacic portion comprises at least 50 phr of a polybutadiene having a content of cis-1,4 bonds of greater than 90%.

15. The tire according to any one of Claims 1 to 14, wherein the reinforcing filler comprises an inorganic filler or a carbon black or a mixture thereof.

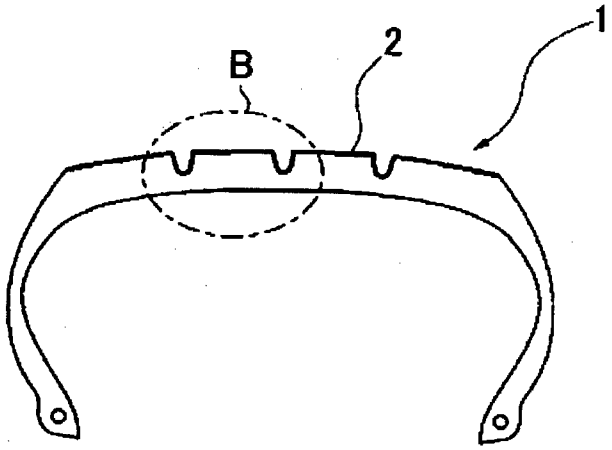
16. The tire according to any one of Claims 1 to 15, wherein the content of total reinforcing filler is between 60 and 120 phr.

17. The tire according to any one of Claims 1 to 16, wherein the liquid plasticizer is chosen from the group consisting of 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.

18. The tire according to Claim 17, wherein the content of liquid plasticizer is greater than 40 phr.

FIG.1

(a)



(b)

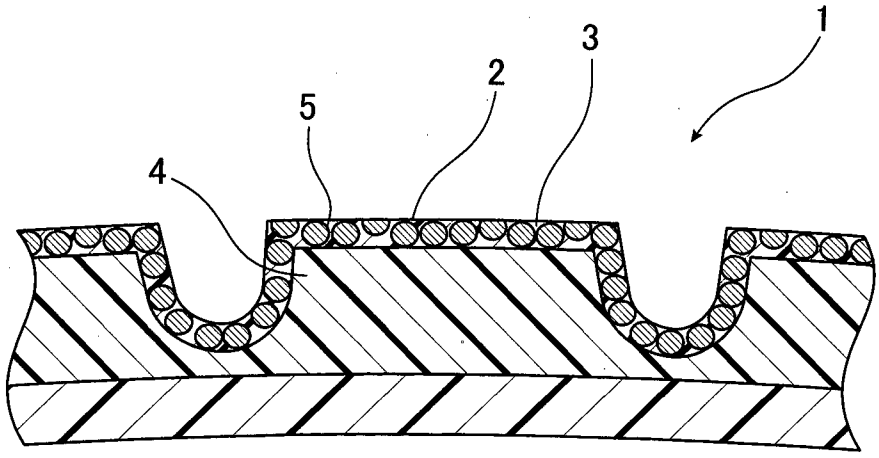
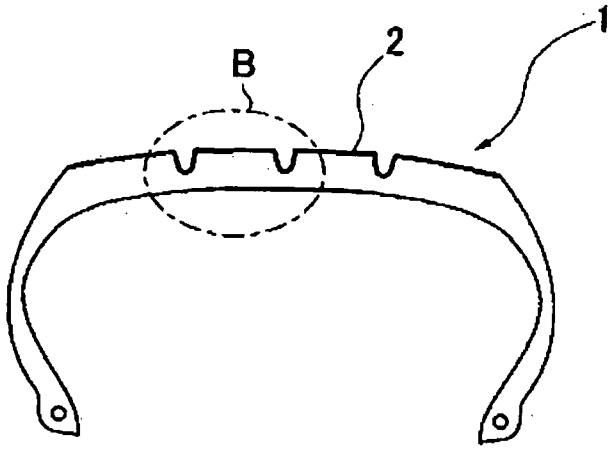
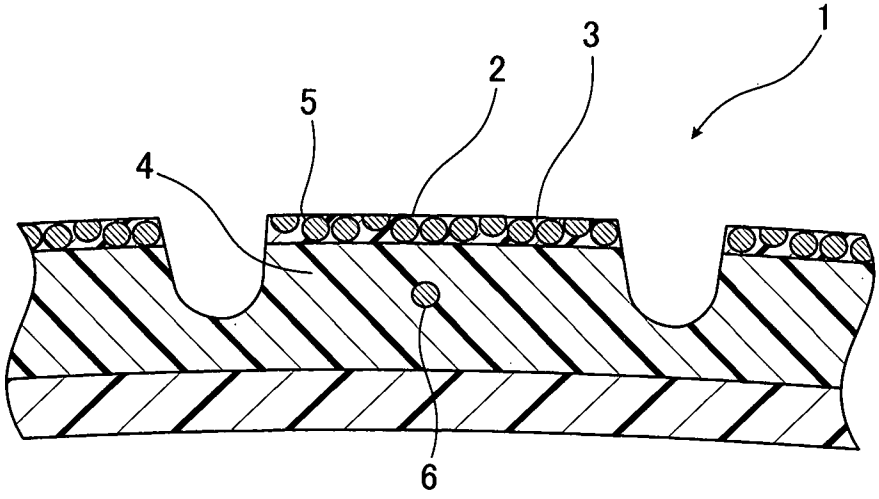


FIG.2

(a)



(b)



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2014/070801

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. B60C11/14(2006.01)i, B60C11/00(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. B60C11/14, B60C11/00

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 1971-2014
Registered utility model specifications of Japan 1996-2014
Published registered utility model applications of Japan 1994-2014

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.
Y	Microfilm of the specification and drawings annexed to the written application of Japanese Utility Model Application No.40070/1990 (Laid-open No.130703/1991) (KANEKO, Sachio) 1991.12.27, claims 1 to 2, page 5, line 16 to page 6, line 6, page 6, line 15 to page 14, line 6, figures 1 to 2 (Family: none)	1-18
Y	JP 2013-514398 A (COMPANY GENERAL DE ETABLISMAN MICHELIN) 2013.04.25, claims 1 to 14, paragraphs [0013] and [0015] & EP 2512825 A1 & WO 2011/073186 A1 & FR 2955584 A1 & CA 2784412 A1	1-18

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

* Special categories of cited documents:
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Date of the actual completion of the international search	Date of mailing of the international search report
14.10.2014	21.10.2014

Name and mailing address of the ISA/JP	Authorized officer	
Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	SUGIZAKI, Satoru Telephone No. +81-3-3581-1101 Ext. 3381	3Q 4854

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2014/070801

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2013-52864 A (THE GOODYEAR TIRE & RUBBER CO.) 2013.03.21, paragraph [0030] & US 2013/0048167 A1 & EP 2565057 A1 & CN 102963215 A	10-11