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(54) Title: A TIRE HAVING A TREAD COMPRISING PARTICLES OF CORK

(57) Abstract: The present invention related to a tire, an unvulcanized state or a vulcanized one, having a tread that comprises a rubber composition. Such rubber composition comprises at least: a diene elastomer, 20 to 100 phr of a plasticizer, 20 to 150 phr of a reinforcing filler, more than 15 phr and less than 100 phr of particles of cork. Said plasticizer is chosen from the group consisting of liquid plasticizers, hydrocarbon resins and the mixtures thereof. In the vulcanized state, said cork particles have a median size by weight of more than 0.5 mm and less than 3 mm. In the vulcanized state, said rubber composition has a dencity of from 0.55 to 0.96g/cm^3. The present invention makes possible a better anti-noise performance, especially regarding the coast-by noise, while maintaining or even improving the stability performance of the tire.

WO 2016/002967 A1

DESCRIPTION

Title of Invention

A TIRE HAVING A TREAD COMPRISING PARTICLES OF CORK

1. FIELD OF THE INVENTION

【0001】

The present invention relates to rubber compositions forming treads of tires, the tires and to a process manufacturing the tires. It relates more particularly to the tires having the treads that comprise the rubber compositions capable to reduce noise from the tires when the vehicle is moving.

2. BACKGROUND

【0002】

A regulation of tire rolling noise emission (Directive 2001/43/EC) was introduced in Europe in 2001, and limits of the tire rolling sound emission level was described in the regulation. The limits were adopted into UN/ECE (United Nations Economic Commission for Europe) Regulation No.117 revision 1 concerning the Approval of Tire with regard to rolling sound emission (called R117-01 below) in 2005.

【0003】

The World Forum for Harmonization of Vehicle Regulations in UN/ECE (WP.29) adopted the revision 2 (called R117-02 below) in 2010. Limits in R117-02 are more severe than that in R117-01 by about 4 dB(A). R117-02 has been implemented in Europe since 2012 and several countries and zones are going to ratify R117-02.

Therefore, there is a constant compelling need for reducing the tire rolling noise emission (called coast-by noise below) in the worldwide.

【0004】

In particular, in order to reduce coast-by noise, tire manufacturers have provided up to now different solutions which consist of modifying the formulation of rubber compositions themselves.

【0005】

It is known that the noise emitted by a tire during rolling originates, inter alia, from the vibrations of its structure following the contact of the tire with the irregularities of the road, also causing a generation of various acoustic waves. The whole is finally perceived in the form of noise, both inside and outside the vehicle. The amplitude of these various manifestations is dependent on the intrinsic modes of vibration of the tire, but also on the nature of the surfacing on which the vehicle is travelling. The range of frequencies corresponding to noise generated by tires extends typically from 20 to 4000 Hz approximately.

【0006】

As regards the noise perceived inside the vehicle, two modes of sound propagation coexist:

- the vibrations are transmitted by the Wheel center, the suspension system and the transmission to finally generate noise in the passenger compartment; this is referred to as solid-route transmission, which is generally dominant for the low frequencies of the spectrum (up to about 400 HZ);

【0007】

- the acoustic waves emitted by the tire are directly propagated via the aerial route into the vehicle, the vehicle acting as a filter; this is referred to as aerial-route transmission, which is generally dominant in the high frequencies (about 600 HZ and above).

【0008】

The noise known as “road noise” rather makes reference to the overall level perceived in the vehicle and over a frequency range of up to 2000 HZ. The noise known as “cavity noise” refers to the nuisance caused by the resonance of the inflation cavity of the tire casing.

【0009】

As regards the noise emitted outside the vehicle, various interactions between the tire and the road surfacing and between the tire and the air are pertinent, and will be a nuisance to people in the vicinity of the vehicle when it is rolling on a road. In this case, several sources of noise are also distinguished, such as the “indentation” noise due to the impact of the unevenness of the road in the area of contact, the “friction” noise essentially generated on leaving the area of contact, the “profile” noise due to the arrangement of the profile elements and to the resonance in the various grooves. The specific range of frequencies concerned by these outside noises corresponds herein typically to a range of from 300 to 3000 HZ approximately.

3. BRIEF DESCRIPTION OF THE INVENTION

【0010】

The objective of the invention is to provide a tire having treads that can reduce the coast-by noise, while at least maintaining or even improving the stability performance.

Now, the applicants have discovered a novel and specific rubber composition for a tire tread which makes it possible to achieve the above objective, that is to say to reduce the coast-by noise, while at least maintaining or even improving the stability performance.

【0011】

Thus, a first subject matter of the present invention is a tire, in an unvulcanized state or a vulcanized one, having a tread that comprises a rubber composition comprising at least, a diene elastomer, 20 to 100 phr of a plasticizer chosen from the group consisting of liquid plasticizers, hydrocarbon resins and the mixtures thereof, 20 to 150 phr of a reinforcing filler, more than 15 phr and less than 100 phr of particles of cork, wherein in the vulcanized state, the median size by weight of said particles is more than 0.5 mm and less than 3 mm and the density of the rubber composition is from 0.55 to 0.96 g/cm^3.

【0012】

Moreover, aspects of the present invention can be as follows.

[1] A tire, in an unvulcanized state or a vulcanized one, having a tread that comprises a rubber composition comprising at least:

- a diene elastomer;
- 20 to 100 phr of a plasticizer chosen from the group consisting of liquid plasticizers, hydrocarbon resins and the mixtures thereof;
- 20 to 150 phr of a reinforcing filler;
- more than 15 phr and less than 100 phr of particles of cork;

wherein:

in the vulcanized state, the median size by weight of said particles is more than 0.5 mm and less than 3 mm and the density of the rubber composition is from 0.55 to 0.96 g/cm^3.

[2] The tire according to [1], wherein the content of the particles is within a range from 20 to 80 phr, preferably within a range from 20 to 60 phr.

[3] The tire according to [1] or [2], wherein the density of the rubber composition in a vulcanized state is from 0.60 to 0.94 g/cm^3, preferably from 0.66 to 0.92 g/cm^3.

[4] The tire according to any one of [1] to [3], wherein the median size by weight is between 0.7 and 3 mm, preferably between 1 and 3 mm.

[5] The tire according to any one of [1] to [4], wherein the particles are in the form of a powder, microbeads, granules, balls or mixtures thereof.

[6] The tire according to [5], wherein the particles are in the form of granules.

[7] The tire according to any one of [1] to [6], wherein the particles are particles of natural cork.

[8] The tire according to any one of [1] to [7], wherein the diene elastomer is chosen from the group consisting of natural rubber, synthetic polyisoprenes, polybutadienes, butadiene copolymers, isoprene copolymers and the mixtures thereof.

[9] The tire according to any one of [1] to [8], wherein the rubber composition comprises 50 to 100 phr of a copolymer based on styrene and butadiene, and 0 to 50 phr of another optional diene elastomer.

[10] The tire according to [9], wherein the copolymer based on styrene and butadiene is chosen from the group consisting of styrene-butadiene copolymers, styrene-butadiene-isoprene copolymers and the mixtures thereof.

[11] The tire according to [9], wherein the copolymer based on styrene and butadiene is a styrene-butadiene copolymer (SBR).

[12] The tire according to any one of [9] to [11], wherein the copolymer based on styrene and butadiene has a glass transition temperature at greater than -40 °C.

[13] The tire according to [12], wherein the copolymer based on styrene and butadiene has a glass transition temperature within a range from -30 °C to +30°C.

[14] The tire according to any one of [9] to [13], wherein the other optional diene elastomer is chosen from the group consisting of natural rubber, synthetic polyisoprenes, isoprene copolymers, and mixtures thereof.

[15] The tire according to any one of [9] to [13], wherein the other optional 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%, and mixtures thereof.

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

[17] The tire according to any one of [1] to [16], wherein the content of the reinforcing filler is from 50 to 120 phr, preferably from 70 to 100phr.

[18] The tire according to any one of [1] to [17], wherein the plasticizer comprises liquid plasticizers 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.

[19] The tire according to any one of [1] to [18], wherein the plasticizer comprises hydrocarbon resins chosen from the group consisting of cyclopentadiene homopolymer or copolymer resins, dicyclopentadiene homopolymer or copolymer resins, terpene homopolymer or copolymer resins, C5 fraction homopolymer or copolymer resins, C9 fraction homopolymer or copolymer resins, alpha-methyl styrene homopolymer or copolymer resins, and the mixtures of these resins.

[20] The tire according to any one of [1] to [19], wherein the content of the plasticizer is from 20 to 80phr, preferably from 25 to 75 phr.

[21] The tire according to any one of [1] to [20], wherein a median size of the particles before incorporated in the diene elastomer is between 0.7 and 4 mm.

[22] A process of manufacturing the tire according to any one of [1] to [21], comprising at least the steps of:

- incorporating in at least a diene elastomer, into a mixer;
- 20 to 100 phr of a plasticizer chosen from the group consisting of liquid plasticizers, hydrocarbon resins and the mixtures thereof
- 20 to 150 phr of a reinforcing filler
- More than 15 phr and less than 100 phr of particles of cork, said particles having a median size by weight of between 0.7 and 4 mm;

everything being kneading thermomechanically, in one or more goes, until a maximum temperature of between 130° C and 200° C 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 a form of a tread of the tire.

[23] A process of manufacturing the tire according to [22], further comprising a final vulcanization step of the tire once manufactured, wherein said vulcanization step is carried out at a vulcanization pressure less of than 1.6 MPa.

[24] A rubber composition comprising at least:

- a diene elastomer;
- 20 to 100 phr of a plasticizer chosen from the group consisting of liquid plasticizers, hydrocarbon resins and the mixtures thereof;
- 20 to 150 phr of a reinforcing filler;
- more than 15 phr and less than 100 phr of particles of cork;

wherein:

in the vulcanized state, the median size by weight of said particles is more than 0.5 mm and less than 3 mm and the density of the rubber composition is from 0.55 to 0.96 g/cm^3.

【0013】

The tires of the present invention are particularly intended to equip passenger motor vehicles, including 4×4 (four-wheel drive or all-wheel drive) vehicles and SUV (Sport Utility Vehicles) vehicles, two-wheel vehicles (in particular motorcycles), and also industrial vehicles in particular chosen from vans and heavy-duty vehicles (i.e., underground vehicles, bus vehicles or heavy road transport vehicles (lorries, tractors, trailers)), or off-road vehicles, such as agricultural vehicles or earthmoving equipment.

【0014】

The invention and its advantages will be easily understood in the light of the description and implementation examples which follow.

4. MEASUREMENTS AND TESTS USED

【0015】

The rubber compositions and the tires according to the present invention including Examples are characterized and tested as indicated below.

4-1. Tensile tests

【0016】

These tensile tests make it possible to determine the elasticity stresses and the properties at break. Unless otherwise indicated, they are carried out in accordance with French Standard NF T 46-002 of September 1988. The nominal secant moduli (or apparent stresses, in MPa) are measured in second elongation (i.e., after a cycle of accommodation to the degree of extension expected for the measurement itself) at 10% elongation (denoted by M10). All these tensile measurements are carried out under the standard conditions of temperature (23 ± 2°C) and hygrometry (50 ± 5% relative humidity), according to French Standard NF T 40-101 (December 1979).

4-2. Machine rolling test on a tire with regard to rolling sound emission

【0017】

The machine rolling test was performed by placing in contact (each tire under an inflation pressure (180 kPa) of the tire mounted on a rim (6.5Jx16) and subjected to a load (4.25 kN)) on the outer surface of a cylinder provided with a rough surface. The assembly is placed in a soundproof chamber (semi-anechoic). Several microphones are placed around the contact area to record the sound level during rolling, over a range of frequencies ranging from 500 to 2500 Hz, for a rolling speed (80km/hour).

5. DETAILED DESCRIPTION OF THE INVENTION

【0018】

The abbreviation "phr" means parts by weight per 100 parts of elastomer. 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).

5-1. Diene elastomer

【0019】

The tread of the tire according to the present invention comprises a rubber composition which has an essential feature of comprising a diene elastomer.

【0020】

It should be remembered that “diene” elastomer or rubber should be understood 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).

【0021】

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 of 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%.

【0022】

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 of these elastomers. 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 of such copolymers.

【0023】

More preferably, the rubber composition composing the tread of the tire of the present invention comprises, as the diene elastomer, from 50 to 100 phr of a copolymer based on styrene and on butadiene, that is to say a copolymer of at least one styrene monomer and of at least one butadiene monomer; in other words, said copolymer based on styrene and on butadiene comprises, by definition, at least units derived from styrene and units derived from butadiene.

【0024】

Still more preferably, the content of said copolymer in the rubber composition is within a range from 50 to 90 phr, particularly within a range from 60 to 85 phr.

【0025】

Suitable butadiene monomers are in particular 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 and an aryl-1,3-butadiene. Suitable styrene monomers are in particular styrene, methylstyrenes, para-(tert-butyl)styrene, methoxystyrenes and chlorostyrenes.

【0026】

Said copolymer based on styrene and on butadiene may have any microstructure, which is a function of the polymerization conditions used, in particular of the presence or absence of a modifying and/or randomizing agent and of the amounts of modifying and/or randomizing agents used. It may be, for example, a block, statistical, sequential or microsequential copolymer, and may be prepared in dispersion or in solution; it may be coupled and/or star-branched or else functionalized with a coupling and/or star-branching or functionalizing agent.

【0027】

Preferably, the copolymer based on styrene and on butadiene is chosen from the group consisting of styrene-butadiene (abbreviated to SBR) copolymers, styrene-butadiene-isoprene (abbreviated to SBIR) copolymers and blends of such copolymers.

【0028】

Among the SBIR copolymers, mention may especially be made of those having a styrene content between 5% and 50% by weight and more particularly between 10% and 40%, an isoprene content between 15% and 60% by weight and more particularly between 20% and 50%, a butadiene content between 5% and 50% by weight and more particularly between 20% and 40%, a content (mol%) of 1,2- units of the butadiene part of between 4% and 85%, a content (mol%) of trans-1,4- units of the butadiene part of between 6% and 80%, a content (mol%) of 1,2- units plus 3,4- units of the isoprene part of between 5% and 70% and a content (mol%) of trans-1,4- units of the isoprene part of between 10% and 50%.

【0029】

More preferably, an SBR copolymer is used. Among the SBR copolymers, mention may especially be made of those having a styrene content of between 5% and 60% by weight and more particularly of between 20% and 50%, a content (mol%) of 1,2- bonds of the butadiene part of between 4% and 75% and a content (mol%) of trans-1,4- bonds of between 10% and 80%.

【0030】

The Tg (glass transition temperature) of copolymer based on styrene and on butadiene is preferably greater than -40°C, more preferably greater than -35°C, particularly within a range from -30°C to +30°C, more particularly within a range from -25°C to +25°C.

【0031】

The Tg of the elastomers described here is measured in a conventional manner, well known to a person skilled in the art, on an elastomer in the dry state (i.e. without extender oil) and by DSC (*Differential Scanning Calorimetry*) (for example according to ASTM D3418 (1999)).

【0032】

A person skilled in the art knows how to modify the microstructure of a copolymer based on styrene and on butadiene, in particular of an SBR, in order to increase and adjust its Tg, especially by playing with the contents of styrene, of 1,2- bonds or else of trans-1,4- bonds of the butadiene part. Use is more preferably made of an SBR (solution or emulsion) having a styrene content (mol%) which is greater than 35%, more particularly between 35% and 60%, in particular within a range from 38% to 50%. SBRs having a relatively high Tg are well known to a person skilled in the art; they have been used in particular in tire treads for improving some of their standard properties.

【0033】

With the preferable copolymer based on styrene and on butadiene described above, at least another optional (or second) diene elastomer, optional and different from said copolymer (i.e. not comprising units derived from styrene and butadiene) may be combined, said second diene elastomer being present in a weight content which is consequently at most equal to 50 phr in case of that content of copolymer based on styrene and on butadiene is at least equal to 50 phr. That means content of the other diene elastomer(s) is 100 phr minus that of copolymer based on styrene and on butadiene.

【0034】

This optional second diene elastomer is preferably chosen from the group consisting of natural rubbers (NR), synthetic polyisoprenes (IR), polybutadienes (BR), isoprene copolymers and blends of these elastomers. Such copolymers are more preferably chosen from the group consisting of isoprene-butadiene copolymers (BIR) and isoprene-styrene copolymers (SIR).

【0035】

Especially suitable, among the latter, are polybutadiene (BR) homopolymers and in particular those having a content (mol%) of 1,2- units of between 4% and 80% or those having a content (mol%) of cis-1,4- units of greater than 80%; polyisoprene (IR) homopolymers; butadiene-isoprene copolymers (BIR) and especially those having an isoprene content of between 5% and 90% by weight and a Tg from -40°C to -80°C; and isoprene-styrene copolymers (SIR) and especially those having a styrene content of between 5% and 50% by weight and a Tg of between -25°C and -50°C.

【0036】

According to one preferred embodiment, the second diene elastomer is an isoprene elastomer, more preferably natural rubber or a synthetic polyisoprene of cis-1,4-type; among these synthetic polyisoprenes, use is preferably made of polyisoprenes having a content (mol%) of cis-1,4- bonds of greater than 90%, more preferably still of greater than 98%.

【0037】

According to another more preferred embodiment, the second diene elastomer is a polybutadiene, preferably a polybutadiene having a content (mol%) of cis-1,4 bonds of greater than 90%.

【0038】

According to another more preferred embodiment, the second diene elastomer is a mixture of polybutadiene with the following isoprene elastomer (natural rubber or synthetic polyisoprene).

5-2. Plasticizing system

【0039】

The rubber composition of the tread of the tire according to the present invention, as another essential feature, comprises a plasticizer chosen from the group consisting of liquid plasticizers, (solid) hydrocarbon resins and the mixtures thereof, within a range from 20 to 100 phr.

【0040】

Liquid plasticizers are liquid at 20°C by definition , their role is to soften the matrix by diluting the elastomer and the reinforcing filler; their Tg is by definition less than -20°C, preferably less than -40°C.

【0041】

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.

【0042】

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.

【0043】

According to a preferred embodiment, the liquid plasticizer is chosen from the group consisting of MES oils, TDAE oils, naphthenic oils, vegetable oils and the mixtures thereof.

【0044】

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.

【0045】

Hydrocarbon resins, which are solid plasticizers (at 20°C), exhibit 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.

【0046】

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 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.

【0047】

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).

【0048】

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").

【0049】

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, alpha-methyl styrene 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/vinyl-aromatic copolymer resins, C_9 fraction/vinylaromatic copolymer resins, and the mixtures thereof.

【0050】

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.

【0051】

The content of total plasticizing agent is preferably from 20 to 80 phr and more preferably from 25 to 75 phr.

5-3. Reinforcing filler

【0052】

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.

【0053】

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 nm and 200 nm, in particular and preferably between 20 nm and 150 nm.

【0054】

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, 300, 600 or 700 series (ASTM grades), such as, for example, the N115, N134, N234, N326, N330, N339, N347, 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).

【0055】

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.

【0056】

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.

【0057】

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.

【0058】

The rubber composition of the tread of the tire according to the present invention, as another essential feature, comprises a reinforcing filler (in particular silica or carbon black or a mixture of silica and carbon black) within a range from 20 to 150 phr. Beyond the maximum, there is a risk of increasing the hysteresis and thus the rolling resistance of the tires. For this reason, the total content of reinforcing filler is preferably within a range from 50 to 120 phr, more preferably within a range from 70 to 100 phr.

【0059】

According to a 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 between 70 and 120 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 15 phr, more preferably less than 10 phr (for example between 0.1 and 10 phr).

【0060】

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.

【0061】

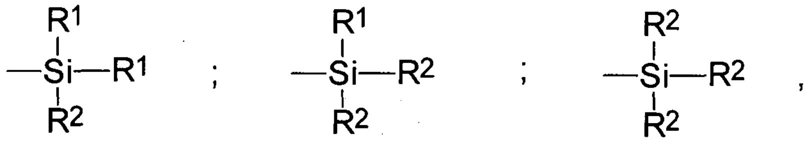
Use is made in particular of silane polysulphides, referred to as “symmetrical” or “asymmetrical” depending on their specific structure, as described, for example, in Applications WO 03/002648 (or US 2005/016651) and WO 03/002649 (or US 2005/016650).

【0062】

“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:



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

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.

【0063】

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

【0064】

Mention will more particularly be made, as examples of silane polysulphides, of bis((C_1-C_4)alkoxyl(C_1-C_4)alkylsilyl(C_1-C_4)alkyl)polysulphides (in particular disulphides, trisulphides or tetrasulphides), such as, for example, bis(3-trimethoxysilylpropyl) or bis(3-triethoxysilylpropyl)polysulphides. Use is in particular made, among these compounds, of bis(3-triethoxysilylpropyl)tetrasulphide, abbreviated to TESPT, of formula $[(C_2H_5O)_3Si(CH_2)_3S_2]_2$, or bis(3-triethoxysilylpropyl)disulphide, abbreviated to TESPD, of formula $[(C_2H_5O)_3Si(CH_2)_3S]_2$. 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).

【0065】

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.

【0066】

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.

【0067】

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.

【0068】

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

【0069】

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.

5-4. Particles of cork

【0070】

The rubber composition of the tread of the tire according to the present invention, as another essential feature, comprises cork particles within a range of more than 15 phr and less than 100 phr, said particles having a median size by weight of more than 0.5 mm and less than 3 mm in the vulcanized (or cured) state.

【0071】

Below the indicated minimum, the targeted technical effect is insufficient, where above the recommended maximum, there is a risk of worsening wear resistance of the tire. For this reason, this content is preferably within a range from 20 to 80 phr, more preferably within a range from 20 to 60 phr, still more preferably within a range from 20 to 50 phr.

【0072】

The median size by weight of the particles of cork in the vulcanized state is more than 0.5 mm and less than 3 mm. Below the indicated minimum, the targeted technical effect is insufficient, where above the recommended maximum, there is a risk too of worsening wear resistance of the tire. For this reason, the median size by weight in the vulcanized state is preferably between 0.7 and 3 mm, more preferably between 1 and 3 mm.

【0073】

Preferably, the particles of cork are in the form of a powder, microbeads, granules, balls or mixtures thereof. More preferably, the particles are in the form of granules due in particular to an easy availability.

【0074】

Preferably, cork is natural cork.

【0075】

For analysis of size of particles and calculation of median of the size (or diameter) of the particles after curing (that is, in the vulcanized state), various known methods can be applied, for example via laser scattering (for example according to ISO-8130-13 or JIS K5600-9-3) or image analysis from optical or electron microscopes or from photomicrographs (for example according to ISO-13322-1 or JIS Z8827-1).

【0076】

The median diameter (or median size) by weight is ultimately calculated in a known manner starting from the distribution of the particle size by number, whatever the form of the particles, said particles being considered as spheres of equivalent volume and density.

5-5. Various additives

【0077】

The rubber composition of the tread of the tire according to the present invention can comprise all or a portion of the usual additives generally used in the elastomer compositions intended for the manufacture of treads for tires, such as, for example, pigments, protection agents, such as antiozone waxes, chemical antiozonants, antioxidants, antifatigue agents, reinforcing resins, such as 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.

【0078】

The rubber composition 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.

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

【0079】

The rubber compositions composing the tread of the present invention is 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.

【0080】

A process which can be used for the manufacture of such compositions forming the tread of the tire according to the present invention comprises, for example and preferably, the following steps:

- incorporating in the diene elastomer, into a mixer, at least the plasticizer, the reinforcing filler, the particles of cork, 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 the form of the tread of the tire.

【0081】

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.

【0082】

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 5.0 phr, and that of the primary accelerator is preferably between 0.5 and 8.0 phr.

【0083】

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-benzothiazole-sulphenamide (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.

【0084】

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 tire tread.

【0085】

The density (or specific gravity) of the rubber composition of the tread of the tire is from 0.55 to 0.96 g/cm^3 in the vulcanized state. Above the indicated maximum, the targeted technical effect (noise reduction) is insufficient, where below the recommended minimum, there is a risk of worsening wear of the tire. For this reason, this content is preferably within a range from 0.60 to 0.94 g/cm^3 and more preferably within a range from 0.66 to 0.92 g/cm^3.

【0086】

Various known methods are applicable for the measurement of the above density (specific gravity). For example, hydrostatic method (see, for example ISO-2781, ASTM D297 and ASTM D792).

【0087】

According to a preferred embodiment, the vulcanization (or curing) is carried out a specific way at a vulcanization (or curing) pressure of less than 1.6 MPa (notably between 0.2 and 1.6 MPa) for a sufficient time which can vary, for example, between 5 and 90 min depending in particular on the vulcanization pressure, the vulcanization system adopted and the vulcanization kinetics of the composition under consideration, which may prevent from excessively decreasing the median size by weight of the particles of cork and increasing the density of rubber composition of the tread of the tire.

【0088】

The vulcanization pressure is preferably less than 1.4 MPa (notably between 0.2 and 1.4 MPa), more preferably at most 1.2 MPa (notably within a range from 0.4 to 1.2 MPa), still more preferably at most 1.0 MPa (notably within a range from 0.5 to 1.0 MPa).

【0089】

According to a more preferred embodiment, the median size by weight of the particles of cork, before being incorporated in the diene elastomer, into a mixer, is within a range of between 0.7 and 4.0 mm, more preferably between 0.9 and 4.0 mm, still more preferably between 1.3 and 4.0 mm.

【0090】

For the measurement of the size of particles and calculation of median size (or diameter) of the particles in their initial state, that is before any incorporation in rubber, it is possible to simply use a particle size analysis via mechanical screening (or sieving) through screens (or sieves) of different diameters.

【0091】

The median diameter (or median size) is ultimately calculated in a known manner from the histogram of the particle size distribution.

【0092】

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

6. EXAMPLES OF THE IMPLEMENTATION OF THE INVENTION

【0093】

Results shown in Table 2 and 3 are obtained by methods of measurements and tests mentioned in “4. MEASUREMENTS AND TESTS USED” unless otherwise instructed.

【0094】

The rubber composition comprising the particles of cork (in these examples, natural cork) described previously can advantageously be used in the treads of tires for any type of vehicle, in particular in pneumatic tyres for passenger vehicles, as demonstrated in the following tests.

【0095】

For the requirements of these tests, six rubber compositions (denoted by C-1, C-2, C-3, C-4, C-5 and C-6) were prepared, the formulation of which is given in Table 1 (content of the various products expressed in phr, the vulcanization pressure expressed in MPa); the vulcanization system is composed of sulphur and sulphenamide.

【0096】

The six compositions based on diene elastomers (BR and SBR blend) are compared, which compositions are reinforced with a blend of silica and carbon black with which is or is not combined a fraction (50 phr) of particles of cork, 30 phr or 70 phr of a plasticizer (that is, oil and resin), according to different vulcanization pressure, 1.6 MPa (as a conventional vulcanization pressure), 1.0 MPa, 0.8 MPa or 0.5MPa, as follows:

- composition C-1: control composition without cork particles, with 30 phr of the plasticizer, vulcanization pressure: 1.6 MPa;
- composition C-2: composition without cork particles, with 70 phr of the plasticizer with the goal to reduce the coast-by noise), vulcanization pressure: 1.6 MPa;
- composition C-3: composition with 50 phr of cork particles, with 30 phr of plasticizer, vulcanization pressure: 1.6 MPa;
- composition C-4: composition according to the present invention, with 50 phr of cork particles, with 30 phr of plasticizer, vulcanization pressure: 1.0 MPa;
- composition C-5: composition according to the present invention, with 50 phr of cork particles, with 30 phr of the plasticizer, vulcanization pressure: 0.8 MPa;
- composition C-6: composition according to the present invention, with 50 phr of cork particles, with 30 phr of the plasticizer, vulcanization pressure: 0.5 MPa.

【0097】

The manufacture of these compositions was carried out in the following manner: the reinforcing fillers (carbon black, silica and its associated coupling agent), the plasticizers, the particles of cork, the diene elastomer (or blend of diene elastomers) and the various other ingredients, with the exception of the vulcanization system (sulphur and Accelerator (11)), were successively introduced into an internal mixer having an initial vessel temperature of approximately 60°C; the mixer was thus approximately 70% full (% by volume). Thermomechanical working (non-productive phase) was then carried out in one stage, which lasts in total approximately 3 to 4 minutes, until a maximum "dropping" temperature of 165°C is reached. The mixture thus obtained was recovered and cooled and then sulphur and an accelerator of sulphenamide type were incorporated on an external mixer (homofinisher) at 30°C, everything being mixed (productive phase) for an appropriate time (for example between 5 and 12 min).

【0098】

The compositions C-1, C-2, C-3, C-4, C-5 and C-6 thus prepared were then used as treads for radial carcass passenger vehicle pneumatic tires, denoted respectively by T-1 (the control tire), T-2, T-3 (the comparative tires) T-4, T-5 and T-6 (the tires in accordance with the present invention), with a size of 205/55 R16 conventionally manufactured and in all respects identical apart from the rubber compositions forming their treads and vulcanization pressures.

【0099】

Table 2 indicates median sizes by weight of the particles of cork in the four compositions (C-3, C-4, C-5 and C-6) after curing of the four corresponding pneumatic tires (T-3, T-4, T-5 and T-6), and also densities and moduli (M10) in extension, which are at the same level for the four compositions after curing of the four pneumatic tires.

【0100】

Each of the median sizes by weight of the particles of cork was calculated starting from the distribution of sizes by number, which was measured via images from photomicroscopes (enlargement of x7) in accordance with ISO-13322-1, on each of transverse cross sections made through each of the four compositions. For this calculation, the particles of this size distribution, whatever their form, where considered as spheres of equivalent volume and density.

【0101】

The densities of the six compositions were measured at 23° C in the standard manner in accordance with Method A in ISO-2781.

【0102】

First of all, results expressed in Table 2 reveal that the median sizes by weight of the particles in the compositions (C-4, C-5 and C-6) in accordance with the present invention are larger than that in the comparative composition (C-3), and the densities of the compositions in accordance with the present invention are lower than that of the comparative composition (C-3); these results clearly show that the median size and the density strongly depend on the fabrication process (vulcanization pressure).

【0103】

Secondly, Table 2 reveals that the compositions comprising the particles of cork (C-3, C-4, C-5 and C-6) in comparison with the control (C-1) already constitutes an unexpected result for a person skilled in the art: we note indeed that moduli (M10) in extension remain constant in spite of high amount of cork, which is favourable to the mechanical behaviour of the tread and thus to the stability performance of the tire.

【0104】

Table 2 shows also another composition (C-2) comprising higher content of the plasticizer than others has lower M10 than others, which is unfavourable to the mechanical behaviour of the tread and thus to the stability performance of the tire.

【0105】

It is in fact only during actual running tests carried out on tires that the unexpected results - in terms of noise reduction - introduced by the present invention are revealed, as clearly shown by the following tire tests.

【0106】

The results from Table 3 express the differences in the recorded sound level between each of the comparative tires (T-2 and T-3) or the tires (T-4, T-5 and T-6) in accordance with the present invention and the control tire (T-1), at a frequency range from 500 to 2500 Hz.

【0107】

These differences are expressed as sound energy (dB(A)) which corresponds to the integration of the sound pressure as a function of the frequency at the frequency range in question, a negative value indicating a reduction in the noise relative to the control tires (T-1).

【0108】

On reading Table 3, it is unexpectedly observed that, at the effective frequency range (500 to 2500Hz) typical of coast-by noise, the tires (T-4, T-5 and T-6) of the present invention emit much less noise than the control tire (T-1), a reduction of from 1.4 to 2.8 dB(A) for example being considered as very significant for a person skilled in the art.

【0109】

Furthermore, the tires (T-4, T-5 and T-6) of the present invention emit less noise than not only the first comparative tire (T-2) with a higher level of plasticizer and devoid of cork, but also the second comparative tire (T-3) using as tread a rubber composition having a higher density (0.98 g/cm^3).

【0110】

Such a result can of course only be attributed to the specific formulation and the density of the tread of the tire of the present invention, particularly to the presence of the particles of cork at the content and the density that are recommended.

【0111】

In conclusion, the results of the tests commented above show that the tread of the tire in accordance with the present invention, comprising in particular a high level of particles of cork, gives the tires a better anti-noise performance, especially regarding the coast-by noise, while maintaining or even improving the stability performance of the tire.

Table 1

Rubber Composition No.:	Ref.	Comparative examples		Examples of the invention		
	C-1	C-2	C-3	C-4	C-5	C-6
BR (1)	25	25	25	25	25	25
SBR (2)	75	75	75	75	75	75
Silica (3)	80	80	80	80	80	80
Coupling agent (4)	6.6	6.6	6.6	6.6	6.6	6.6
Particles (5)	-	-	50	50	50	50
Carbon black (6)	4	4	4	4	4	4
Non aromatic oil (7)	10	30	10	10	10	10
Hydrocarbon resin (8)	20	40	20	20	20	20
ZnO	1	1	1	1	1	1
Stearic acid	2	2	2	2	2	2
Antiozone wax	1.5	1.5	1.5	1.5	1.5	1.5
Antioxidant (9)	1.9	1.9	1.9	1.9	1.9	1.9
DPG (10)	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	1.2	1.2	1.2	1.2	1.2	1.2
Accelerator (11)	1.9	1.9	1.9	1.9	1.9	1.9
Vulcanization pressure (MPa)	1.6	1.6	1.6	1.0	0.8	0.5

(1) BR with 0.3% of 1,2 vinyl; 2.7% of trans; 97% of cis-1,4 (Tg = -105°C);

(2) SBR with 26% of styrene, 74% of butadiene (21% of -1,4 trans, 21% of -1,4 cis and 58% of -1,2) (Tg = -25°C);

(3) Silica “Zeosil 1165MP” from Rhodia;

(4) Coupling agent TESPT (“Si69” from Evonik);

(5) Granular natural cork from ISHII SANSYOU (median size by weight of the particles measured via sieving: 2 mm);

(6) Grade ASTM N234 (Cabot);

(7) MES oil (“Catenex SNR” from Shell)

(8) Hydrocarbon resin C5/C9 type (“Escorez ECR-373” from Exxon)

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

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

(11) N-dicyclohexyl-2-benzothiazolesulphenamide (“Santocure CBS” from Flexsys).

Table 2

Rubber composition No.:	Ref.	Comparative examples		Examples of the invention		
	C-1	C-2	C-3	C-4	C-5	C-6
Median size by weight of particles of cork (mm)	-	-	1.35	1.49	1.54	1.83
Density (g/cm^3)	1.19	1.15	0.98	0.93	0.92	0.88
M10 (MPa)	6	3	8	8	7	7

Table 3

Tire No.:	Ref.	Comparative examples		Examples of the invention		
	T-1	T-2	T-3	T-4	T-5	T-6
Sound pressure level [dB (A)]	0	-0.9	-0.7	-1.4	-1.9	-2.8

CLAIMS

1. A tire, in an unvulcanized state or a vulcanized one, having a tread that comprises a rubber composition comprising at least:

- a diene elastomer;
- 20 to 100 phr of a plasticizer chosen from the group consisting of liquid plasticizers, hydrocarbon resins and the mixtures thereof;
- 20 to 150 phr of a reinforcing filler;
- more than 15 phr and less than 100 phr of particles of cork;

wherein:

in the vulcanized state, the median size by weight of said particles is more than 0.5 mm and less than 3 mm and the density of the rubber composition is from 0.55 to 0.96 g/cm^3.

2. The tire according to Claim 1, wherein the content of the particles is within a range from 20 to 80 phr.

3. The tire according to Claim 1 or Claim 2, wherein the density of the rubber composition in a vulcanized state is from 0.60 to 0.94 g/cm^3.

4. The tire according to any one of Claims 1 to 3, wherein the median size by weight is between 0.7 and 3 mm.

5. The tire according to any one of Claims 1 to 4, wherein the particles are in the form of a powder, microbeads, granules, balls or mixtures thereof.

6. The tire according to Claim 5, wherein the particles are in the form of granules.

7. The tire according to any one of Claims 1 to 6, wherein the particles are particles of natural cork.

8. The tire according to any one of Claims 1 to 7, wherein the diene elastomer is chosen from the group consisting of natural rubber, synthetic polyisoprenes, polybutadienes, butadiene copolymers, isoprene copolymers and the mixtures thereof.

9. The tire according to any one of Claims 1 to 8, wherein the rubber composition comprises 50 to 100 phr of a copolymer based on styrene and butadiene, and 0 to 50 phr of another optional diene elastomer.

10. The tire according to Claim 9, wherein the copolymer based on styrene and butadiene is chosen from the group consisting of styrene-butadiene copolymers, styrene-butadiene-isoprene copolymers and the mixtures thereof.

11. The tire according to Claim 9, wherein the copolymer based on styrene and butadiene is a styrene-butadiene copolymer (SBR).

12. The tire according to any one of Claims 9 to 11, wherein the copolymer based on styrene and butadiene has a glass transition temperature at greater than -40 °C.

13. The tire according to Claim 12, wherein the copolymer based on styrene and butadiene has a glass transition temperature within a range from -30 °C to +30°C.

14. The tire according to any one of Claims 9 to 13, wherein the other optional diene elastomer is chosen from the group consisting of natural rubber, synthetic polyisoprenes, polybutadienes, isoprene copolymers, and mixtures thereof.

15. The tire according to any one of Claims 9 to 13, wherein the other optional diene elastomer is chosen from the group consisting of natural rubber, synthetic polyisoprenes, polybutadienes, isoprene copolymers having a content of cis-1,4 bond of greater than 90%, and mixtures thereof.

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

17. The tire according to any one of Claims 1 to 16, wherein the content of the reinforcing filler is from 50 to 120 phr, preferably from 70 to 100phr.

18. The tire according to any one of Claims 1 to 17, wherein the plasticizer comprises liquid plasticizers 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.

19. The tire according to any one of Claims 1 to 18, wherein the plasticizer comprises hydrocarbon resins chosen from the group consisting of cyclopentadiene homopolymer or copolymer resins, dicyclopentadiene homopolymer or copolymer resins, terpene homopolymer or copolymer resins, C_5 fraction homopolymer or copolymer resins, C_9 fraction homopolymer or copolymer resins, alpha-methyl styrene homopolymer or copolymer resins, and the mixtures of these resins.

20. The tire according to any one of Claims 1 to 19, wherein the content of the plasticizer is from 20 to 80phr.

21. The tire according to any one of Claims 1 to 20, wherein a median size of the particles before incorporated in the diene elastomer is between 0.7 and 4 mm.

22. A process of manufacturing the tire according to any one of Claims 1 to 21, comprising at least the steps of:

- incorporating in at least a diene elastomer, into a mixer;
  - o 20 to 100 phr of a plasticizer chosen from the group consisting of liquid plasticizers, hydrocarbon resins and the mixtures thereof

  - o 20 to 150 phr of a reinforcing filler
  - o More than 15 phr and less than 100 phr of particles of cork, said particles having a median size by weight of between 0.7 and 4 mm;

  everything being kneading thermomechanically, in one or more goes, until a maximum temperature of between 130° C and 200° C 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 a form of a tread of the tire.

23. A process of manufacturing the tire according to claim 22, further comprising a final vulcanization step of the tire once manufactured, wherein said vulcanization step is carried out at a vulcanization pressure of less than 1.6 MPa.

24. A rubber composition comprising at least:

- a diene elastomer;
- 20 to 100 phr of a plasticizer chosen from the group consisting of liquid plasticizers, hydrocarbon resins and the mixtures thereof;
- 20 to 150 phr of a reinforcing filler;
- more than 15 phr and less than 100 phr of particles of cork;

wherein:

in the vulcanized state, the median size by weight of said particles is more than 0.5 mm and less than 3 mm and the density of the rubber composition is from 0.55 to 0.96 g/cm^3.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/069369

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C08L9/00(2006.01)i, B60C1/00(2006.01)i, C08K3/02(2006.01)i, C08K3/36(2006.01)i, C08L91/00(2006.01)i, C08L97/02(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. C08L7/00-21/02, B60C1/00, C08K3/00-13/08, C08L91/00, C08L97/02

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 1971-2015
Registered utility model specifications of Japan 1996-2015
Published registered utility model applications of Japan 1994-2015

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

CAplus/REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 368411 A (EWALD GOLTSTEIN) 1932.03.10, whole document & FR 713120 A & BE 368411 A	1-24
A	JP 2007-506609 A (CARCOUSTICS TECH CENTER GMBH) 2007.03.22, whole document & US 2006/0144627 A1 & WO 2005/007458 A1 & EP 1644222 A1 & DE 10332172 B & CN 1705576 A	1-24
A	JP 2-167353 A (SUMITOMO RUBBER INDUSTRIES, LTD.) 1990.06.27, whole document & US 5049598 A & US 5246985 A & EP 332459 A1	1-24

☑ 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
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"P" document published prior to the international filing date but later than the priority date claimed
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"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
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/069369

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 9-278941 A (SUMITOMO BAKELITE CO., LTD.) 1997.10.28, whole document (No Family)	1-24
A	JP 8-269242 A (TOYODA GOSEI CO., LTD.) 1996.10.15, whole document (No Family)	1-24