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(54) Title: PEROXIDE CURED TREAD

(57) Abstract: A tire tread manufactured at least in part from a rubber composition that is based upon a cross-linkable elastomer composition comprising between 80 phr and 100 phr of a polybutadiene-based elastomer modified with a functional group that is capable of interacting with a silica reinforcing filler, wherein a polybutadiene portion of the polybutadiene-based elastomer has between 8 wt% and 15 wt% vinyl units, wherein the polybutadiene-based elastomer includes at least 30 mol% *trans*-bonds and wherein the polybutadiene-based elastomer has a glass transition temperature of between -100° C and -80° C. Such rubber composition is cured with a peroxide curing agent.

PEROXIDE CURED TREAD

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] This invention relates generally to passenger and light truck tires and more particularly to treads and materials from which they are made.

Description of the Related Art

[0002] It is known in the industry that tire designers must compromise on certain characteristics of the tires they are designing. Changing a tire design to improve one characteristic of the tire will often result in a compromise, *i.e.,* an offsetting decline in another tire characteristic. One such compromise exists between wet braking and snow traction. Wet braking may be improved by increasing filler loading, decreasing filler particle size and increasing the mix glass transition temperature (Tg). However, these actions typically result in a loss of snow traction performance that is known to be improved by, for example, decreasing filler loading, increasing filler particle size and decreasing mix Tg.

[0003] Making changes in tire design parameters can also change other characteristics such as wear and rolling resistance. Both of these characteristics are important to consumers since they affect the economy of their tire purchase.

[0004] Tire designers and those conducting research in the tire industry search for materials and tire structures that can break some of the known compromises. It would be desirable to provide new tire designs that break the compromise between wet and snow traction and improve wear.

DETAILED DESCRIPTION OF PARTICULAR EMBODIMENTS

[0005] Particular embodiments of the present invention include tire treads and tires that have improved traction and improved wear. This accomplishment includes improved performance in wet traction and snow traction as well as the improved wear performance of the treads. This has been achieved by using a particular polybutadiene-based functional elastomer, namely one that includes low vinyl content, *i.e.*, low *vinyl*-1,2 bonds making up the

polybutadiene, in a rubber composition that has been cured using a peroxide curing system. Such tires are particularly useful as snow tires or as all-weather tires for passenger cars and/or light trucks and also for summer tires.

[0006] As used herein, "phr" is parts per hundred parts of rubber by weight and is a common measurement in the art wherein components of a rubber composition are measured relative to the total weight of rubber in the composition, *i.e.*, parts by weight of the component per 100 parts by weight of the total rubber(s) in the composition.

[0007] As used herein, elastomer and rubber are synonymous terms.

[0008] As used herein, "based upon" is a term recognizing that embodiments of the present invention are made of vulcanized or cured rubber compositions that were, at the time of their assembly, uncured. The cured rubber composition is therefore "based upon" the uncured rubber composition. In other words, the cross-linked rubber composition is based upon or comprises the constituents of the cross-linkable rubber composition.

[0009] As is known generally, a tire tread is the road-contacting portion of a vehicle tire that extends circumferentially about the tire. It is designed to provide the handling characteristics required by the vehicle; *e.g.*, traction, dry braking, wet braking, cornering and so forth - all being preferably provided with a minimum amount of noise being generated and at a low rolling resistance.

[0010] Treads of the type that are disclosed herein include tread elements that are the structural features of the tread that contact the ground. Such structural features may be of any type or shape, examples of which include tread blocks and tread ribs. Tread blocks have a perimeter defined by one or more grooves that create an isolated structure in the tread while a rib runs substantially in the longitudinal (circumferential) direction and is not interrupted by any grooves that run in the substantially lateral direction or any other grooves that are oblique thereto.

[0011] The radially outermost faces of these tread elements make up the contact surface of the tire tread – the actual surface area of the tire tread that is adapted for making contact with the road as the tire rotates. The total contact surface of the tire tread is therefore the total surface area of all the radially outermost faces of the tread elements that are adapted for making contact with the road.

[0012] Suitable compositions for making the treads and tires disclosed herein include a polybutadiene-based elastomer that has been modified with a functional group that is capable of interacting with a silica reinforcing filler. A polybutadiene-based elastomer means one that is either a homopolymer of butadiene units, such as 1,3-butadiene, or a copolymer of butadiene units and another monomer. In embodiments that include such a copolymer, the copolymer includes at least 95 wt% butadiene units. In particular embodiments the second monomer may be a vinyl aromatic and may be included in an amount of between greater than 0 wt% and 5 wt% or alternatively between 1 wt% and 4 wt%, based on the total weight of the copolymer. In particular embodiments the elastomer may be limited to either a polybutadiene homopolymer rubber (BR) or a styrene-butadiene copolymer (SBR) that is a copolymer of a butadiene and a styrene or combinations thereof. In such copolymers, the styrene content is no more than 4 wt% styrene or alternatively, no more than 3 wt% styrene or between 0.5 wt% and 2 wt% styrene.

[0013] The modified elastomers suitable for particular embodiments of the rubber compositions disclosed herein may be described as having a glass transition temperature of no greater than -80° C or alternatively between -100° C and -80° C or between -95° C and -80° C. Glass transition temperatures for the modified elastomers are determined by differential scanning calorimetry (DSC) according to ASTM E1356.

[0014] Particular embodiments of the rubber compositions include the modified polybutadiene-based elastomers having low vinyl bonds content. Because of the double bond present in the butadiene portion of the butadiene-based elastomer, the butadiene portion is made up of three forms: *cis*-1,4, *trans*-1,4 and *vinyl*-1,2. The butadiene-based elastomer, having a low vinyl content, may have a *vinyl*-1,2 content of between 8 wt% and 15 wt% based on the total weight of the polybutadiene portion or alternatively between 10 wt% and 15 wt%. The elastomers may also have a low *cis*-1,4 content and described as having a mole ratio of *cis*-1,4 bonds to *trans*-1,4 bonds of between 1 and 0.65

[0015] Such functionalized elastomers are known, an example of which may be found in pending French patent application 15/59593 filed on October 8, 2015 and which is fully incorporated herein by reference for all that it teaches. This application discloses a modified polybutadiene elastomer functionalized mid-chain with an alkoxysilane functional

group bonded mid-chain into the elastomer chain through the silicon atom. A mid-chain functionalized elastomer can be distinguished from an elastomer that is functionalized at the chain end even though the mid-chain functional group is not located precisely in the middle of the elastomer chain. The application further discloses a polybutadiene having *vinyl*-1,2 bonds of between 8 wt% and 15 wt% as well as having a molar ratio of *cis*-1,4 bonds/*trans*-1,4 bonds of from 1 to 0.65.

[0016] As is known, the alkoxysilane that has been hydrolyzed is capable of reacting with the silica reinforcing filler, a general form of such hydrolyzed moiety being, for example, SiOH. It is further disclosed that the alkoxysilane functional groups, which may be at least partially hydrolyzed or not, may include another functional group capable of interacting with the silica reinforcing filler, such functional moiety being, for example, a primary, secondary or tertiary amino moiety, whether cyclical or not. Such amino moieties may include, for example, diethylamine or dimethylamine.

[0017] Such functional moieties may be positioned in the chain and in particular embodiments, both may be positioned in the chain and actually be within the chain. Alternatively such moieties may be positioned at the chain ends.

[0001] In addition to the rubber components described above, the rubber composition suitable for the tire treads disclosed herein may further include a plasticizing system. The plasticizing system provides both an improvement to the processability of the rubber mix and a means for adjusting the rubber composition's dynamic shear modulus and glass transition temperature. Suitable plasticizing systems include both a plasticizing liquid and a plasticizing resin to achieve the desired braking and snow traction characteristics of the tread.

[0002] Suitable plasticizing liquids may include any liquid known for its plasticizing properties with diene elastomers. At room temperature (23 °C), these liquid plasticizers or these oils of varying viscosity are liquid as opposed to the resins that are solid. Examples include those derived from petroleum stocks, those having a vegetable base and combinations thereof. Examples of oils that are petroleum based include aromatic oils, paraffinic oils, naphthenic oils, MES oils, TDAE oils and so forth as known in the industry. Also known are

liquid diene polymers, the polyolefin oils, ether plasticizers, ester plasticizers, phosphate plasticizers, sulfonate plasticizers and combinations of liquid plasticizers.

[0003] Examples of suitable vegetable oils include sunflower oil, soybean oil, safflower oil, corn oil, linseed oil and cotton seed oil. These oils and other such vegetable oils may be used singularly or in combination. In some embodiments, sunflower oil having a high oleic acid content (at least 70 weight percent or alternatively, at least 80 weight percent) is useful, an example being AGRI-PURE 80, available from Cargill with offices in Minneapolis, MN. In particular embodiments of the present invention, the selection of suitable plasticizing oils is limited to a vegetable oil having high oleic acid content.

[0004] The amount of plasticizing liquid useful in any particular embodiment of the present invention depends upon the particular circumstances and the desired result. In general, for example, the plasticizing liquid may be present in the rubber composition in an amount of between 5 phr and 60 phr or alternatively, between 10 phr and 50 phr, between 10 phr and 40 phr, between 10 phr and 30 phr, between 10 phr and 50 phr or between 12 phr and 30 phr. Since both a plasticizing liquid and a plasticizing hydrocarbon resin are included in the plasticizing system, the amount of both types of plasticizers is adjusted as described below to obtain the desired physical characteristics of the tread.

[0005] A plasticizing hydrocarbon resin is a hydrocarbon compound that is solid at ambient temperature (*e.g.*, 23 °C) as opposed to liquid plasticizing compounds, such as plasticizing oils. Additionally a plasticizing hydrocarbon resin is compatible, *i.e.*, miscible, with the rubber composition with which the resin is mixed at a concentration that allows the resin to act as a true plasticizing agent, *e.g.*, at a concentration that is typically at least 5 phr.

[0006] Plasticizing hydrocarbon resins are polymers/oligomers that can be aliphatic, aromatic or combinations of these types, meaning that the polymeric base of the resin may be formed from aliphatic and/or aromatic monomers. These resins can be natural or synthetic materials and can be petroleum based, in which case the resins may be called petroleum plasticizing resins, or based on plant materials. In particular embodiments, although not limiting the invention, these resins may contain essentially only hydrogen and carbon atoms.

[0007] The plasticizing hydrocarbon resins useful in particular embodiment of the present invention include those that are homopolymers or copolymers of cyclopentadiene

(CPD) or dicyclopentadiene (DCPD), homopolymers or copolymers of terpene, homopolymers or copolymers of C_5 cut and mixtures thereof.

[0008] Such copolymer plasticizing hydrocarbon resins as discussed generally above may include, for example, resins made up of copolymers of (D)CPD/ vinyl-aromatic, of (D)CPD/ terpene, of (D)CPD/ C_5 cut, of terpene/ vinyl-aromatic, of C_5 cut/ vinyl-aromatic and of combinations thereof.

[0009] Terpene monomers useful for the terpene homopolymer and copolymer resins include alpha-pinene, beta-pinene and limonene. Particular embodiments include polymers of the limonene monomers that include three isomers: the L-limonene (laevorotatory enantiomer), the D-limonene (dextrorotatory enantiomer), or even the dipentene, a racemic mixture of the dextrorotatory and laevorotatory enantiomers.

[0010] Examples of vinyl aromatic monomers include styrene, alpha- methylstyrene, ortho-, meta-, para-methylstyrene, vinyl-toluene, para-tertiobutylstyrene, methoxystyrenes, chloro-styrenes, vinyl-mesitylene, divinylbenzene, vinylnaphthalene, any vinyl-aromatic monomer coming from the C_9 cut (or, more generally, from a C_8 to C_{10} cut). Particular embodiments that include a vinyl-aromatic copolymer include the vinyl-aromatic in the minority monomer, expressed in molar fraction, in the copolymer.

[0011] Particular embodiments of the present invention include as the plasticizing hydrocarbon resin the (D)CPD homopolymer resins, the (D)CPD/ styrene copolymer resins, the polylimonene resins, the limonene/ styrene copolymer resins, the limonene/ D(CPD) copolymer resins, C_5 cut/ styrene copolymer resins, C_5 cut/ C_9 cut copolymer resins, and mixtures thereof.

[0012] Commercially available plasticizing resins that include terpene resins suitable for use in the present invention include a polyalphapinene resin marketed under the name Resin R2495 by Hercules Inc. of Wilmington, DE. Resin R2495 has a molecular weight of about 932, a softening point of about 135°C and a glass transition temperature of about 91°C. Another commercially available product that may be used in the present invention includes DERCOLYTE L120 sold by the company DRT of France. DERCOLYTE L120 polyterpene-limonene resin has a number average molecular weight of about 625, a weight average molecular weight of about 1010, an Ip of about 1.6, a softening point of about 119°C and has

a glass transition temperature of about 72° C. Still another commercially available terpene resin that may be used in the present invention includes SYLVARES TR 7125 and/or SYLVARES TR 5147 polylimonene resin sold by the Arizona Chemical Company of Jacksonville, FL. SYLVARES 7125 polylimonene resin has a molecular weight of about 1090, has a softening point of about 125° C, and has a glass transition temperature of about 73°C while the SYLVARES TR 5147 has a molecular weight of about 945, a softening point of about 120 °C and has a glass transition temperature of about 71° C.

[0013] Other suitable plasticizing hydrocarbon resins that are commercially available include C_5 cut/ vinyl-aromatic styrene copolymer, notably C_5 cut / styrene or C_5 cut / C_9 cut from Neville Chemical Company under the names SUPER NEVTAC 78, SUPER NEVTAC 85 and SUPER NEVTAC 99; from Goodyear Chemicals under the name WINGTACK EXTRA; from Kolon under names HIKOREZ T1095 and HIKOREZ T1100; and from Exxon under names ESCOREZ 2101 and ECR 373.

[0014] Yet other suitable plasticizing hydrocarbon resins that are limonene/styrene copolymer resins that are commercially available include DERCOLYTE TS 105 from DRT of France; and from Arizona Chemical Company under the name ZT115LT and ZT5100.

[0015] It may be noted that the glass transition temperatures of plasticizing resins may be measured by Differential Scanning Calorimetry (DSC) in accordance with ASTM D3418 (1999). In particular embodiments, useful resins may be have a glass transition temperature that is at least 25° C or alternatively, at least 40° C or at least 60° C or between 25° C and 95° C, between 40° C and 85° C or between 60° C and 80° C.

[0016] The amount of plasticizing hydrocarbon resin useful in any particular embodiment of the present invention depends upon the particular circumstances and the desired result and may be present in an amount of between 5 phr and 100 phr or alternatively, between 30 phr and 60 phr, between 20 phr and 60 phr, between 30 phr and 90 phr, between 30 phr and 55 phr or between 35 phr and 60 phr. As noted above, since both a plasticizing liquid and a plasticizing hydrocarbon resin are included in the plasticizing system, the amount of both types of plasticizers are adjusted as described below to obtain the desired physical characteristics of the tread to improve both the snow traction and braking properties.

[0017] The amount of the plasticizing system is adjusted to provide the rubber composition with a glass transition temperature of between -35 °C and 0 °C and a dynamic modulus G* at 60 °C of between 0.6 MPa and 1.5 MPa or alternatively between 0.65 MPa and 1.2 MPa, between 0.65 MPa and 1.1 MPa, between 0.65 MPa and 1.0 MPa or between 0.7 MPa and 1.0 MPa, both measured in accordance with ASTM D5992-96. As such, the ratio of the amount of liquid plasticizer (phr) to the amount of plasticizing resin (phr) may be adjusted to achieve the desired physical properties of the rubber composition so that the surprising break in the braking-snow traction compromise is achieved. Such ratios may range from between 0.1 and 0.7 or alternatively between 0.2 and 0.5, between 0.2 and 0.6 or between 0.3 and 0.6.

[0018] The rubber compositions disclosed herein are suitable for use in the manufacture of treads and as known to one skilled in the art, the Tg of the cured rubber composition may be adjusted to provide a tread for a tire that is more suitable for a given season. As such the Tg of the rubber compositions may be adjusted around the broad range mentioned above using the plasticizers disclosed to provide a Tg of between -35 °C and -25 °C for winter tires, between -30 °C and -17 °C for all-season tires and between -17 °C and 0 °C for summer tires.

[0019] In addition to the rubber components and the plasticizing system described above, the rubber compositions suitable for the tire treads disclosed herein may further include a silica reinforcing filler. Reinforcing fillers are used extensively in tires to provide desirable characteristics such as tear strength, modulus and wear. The silica may be any reinforcing silica known to one having ordinary skill in the art, in particular any precipitated or pyrogenic silica having a BET surface area and a specific CTAB surface area both of which are less than 450 m^2/g or alternatively, between 30 and 400 m^2/g. Particular embodiments include a silica having a CTAB of between 80 and 200 m^2/g, between 100 and 190 m^2/g, between 120 and 190 m^2/g or between 140 and 180 m^2/g. The CTAB specific surface area is the external surface area determined in accordance with Standard AFNOR-NFT-45007 of November 1987.

[0020] Particular embodiments of the rubber compositions used in the tire treads of the passenger and light truck vehicles have a BET surface area of between 60 and 250 m^2/g or

alternatively, of between 80 and 200 m^2/g. The BET specific surface area is determined in known manner, in accordance with the method of Brunauer, Emmet and Teller described in "The Journal of the American Chemical Society", vol. 60, page 309, February 1938, and corresponding to Standard AFNOR-NFT-45007 (November 1987).

[0021] The silica used in particular embodiments may be further characterized as having a dibutylphthlate (DHP) absorption value of between 100 and 300 ml/100 g or alternatively between 150 and 250 ml/100 g.

[0022] Highly dispersible precipitated silicas (referred to as "HD") are used exclusively in particular embodiments of the disclosed rubber composition, wherein "highly dispersible silica" is understood to mean any silica having a substantial ability to disagglomerate and to disperse in an elastomeric matrix. Such determinations may be observed in known manner by electron or optical microscopy on thin sections. Examples of known highly dispersible silicas include, for example, Perkasil KS 430 from Akzo, the silica BV3380 from Degussa, the silicas Zeosil 1165 MP and 1115 MP from Rhodia, the silica Hi-Sil 2000 from PPG and the silicas Zeopol 8741 or 8745 from Huber.

[0023] Particular embodiments of the present invention include little or no carbon black or other reinforcement fillers. For those embodiments that include adding a silane coupling agent that is commercially available on a carbon black substrate, up to about 50 wt% of the commercial coupling agent weight is carbon black. The rubber compositions having such amounts of carbon black may be characterized as having essentially no carbon black. Some embodiments may include up to 10 phr, or up to 5 phr of carbon black just to provide a typical black coloring of the rubber composition.

[0024] The amount of silica added to the rubber composition disclosed herein is between 90 phr and 150 phr or alternatively between 95 phr and 145 phr, between 100 phr and 135 phr or between 105 phr and 140 phr.

[0025] In addition to the silica added to the rubber composition, a proportional amount of a silane coupling agent is also added to the rubber composition. Such coupling agent is added, for example, at between 5% and 10% of the total amount of silica. The silane coupling agent is a sulfur-containing organosilicon compound that reacts with the silanol groups of the silica during mixing and with the elastomers during vulcanization to provide

improved properties of the cured rubber composition. A suitable coupling agent is one that is capable of establishing a sufficient chemical and/or physical bond between the inorganic filler and the diene elastomer, which is at least bifunctional, having, for example, the simplified general formula "Y-T-X", in which: Y represents a functional group ("Y" function) which is capable of bonding physically and/or chemically with the inorganic filler, such a bond being able to be established, for example, between a silicon atom of the coupling agent and the surface hydroxyl (OH) groups of the inorganic filler (for example, surface silanols in the case of *silica*); X represents a functional group ("X" function) which is capable of bonding physically and/or chemically with the diene elastomer, for example by means of a sulfur atom; T represents a divalent organic group making it possible to link Y and X.

[0026] Examples of suitable sulfur-containing organosilicon silane coupling agents include 3,3'-bis(triethoxysilylpropyl)disulfide and 3,3'-bis(triethoxy-silylpropyl) tetrasulfide. Both of these are available commercially from Degussa as X75-S and X50-S respectively, though not in pure form. Both of these commercially available products include the active component mixed 50-50 by weight with a N330 carbon black. Other examples of suitable silane coupling agents include 2,2'-bis(triethoxysilylethyel)tetrasulfide, 3,3'-bis(tri-t-butoxy-silylpropyl)disulfide and 3,3'-bis(di t-butylmethoxysilylpropyl)tetrasulfide. Examples of silane coupling agents having just one silicon atom in the silane molecule include, for example, 3,3'(triethoxysilylpropyl)disulfide and 3,3' (triethoxy-silylpropyl)tetrasulfide.

[0027] In addition to the rubber components, the plasticizing system and the reinforcing filler described above, the rubber compositions suitable for the tire treads disclosed herein may further be cured by a peroxide curing system. The peroxide curing system, or vulcanization system, provides the cross-linking mechanism for the formation of covalent bonds between the elastomer chains resulting from the decomposition of the peroxide to form radicals and the subsequent crosslink-forming reactions. The peroxide curing system is necessary to provide the break in the compromise between the braking and snow traction as discussed above.

[0028] Examples of suitable peroxide curing agents include di-cumyl peroxide; tert-butyl cumyl peroxide; 2,5-dimethyl-2,5 bis(tertbutyl peroxy)hexyne-3; bis(tert-butyl peroxy isopropyl)benzene; 4,4-di-tert-butyl peroxy N-butyl valerate; 1,1-di-tert-butylperoxy-3,3,5-

trimethylcyclohexane; bis-(tert-butyl peroxy)-diisopropyl benzene; t-butyl perbenzoate; di-tert-butyl peroxide; 2,5-dimethyl-2,5-di-tert-butylperoxide hexane, as well as other peroxides known to those having ordinary skill in the art and combinations thereof. Such peroxides are available, for example, as VUL-CUP-R, which is α, α'- bis-(tert-butyl peroxy)-diisopropyl benzene and DI CUP, which is di-cumyl peroxide, both available from Arkema having offices in Philadelphia, PA.

[0029] The peroxide curing agent may be added to the rubber composition in an effective amount such as between 0.8 phr and 2.4 phr of active peroxide or alternatively between 1 phr and 2 phr. Since the peroxide products often include inactive ingredients added to the active peroxide, the amount of peroxide disclosed is the amount of active peroxide that should be added to the useful rubber compositions.

[0030] In addition to the peroxide curing agent, a coagent may also be included in the peroxide curing package for particular embodiments of the rubber compositions disclosed herein. Coagents affect the cross-linking efficiency and may improve the properties of the cured rubber compositions.

[0031] Useful curing coagents include those that are non-ionic. Such coagents are known to typically contribute to the state of the cure of the vulcanized rubber and form radicals typically through hydrogen abstraction. Examples of non-ionic coagents include, for example, allyl-containing cyanurates, isocyanurates and phthalates, homopolymers of dienes and copolymers of dienes and vinyl aromatics, such as triallyl cyanurates, triallyl isocyanurate, 90% vinyl polybutadiene and 70% vinyl styrene-butadiene copolymer. RICON 153 is available from Cray Valley (with offices in Exton, PA) and is 85% 1, 2 vinyl polybutadiene, a useful non-ionic coagent having a number average MW of 4700. Any of these coagents may be used singly or in combinations with one or more of the others.

[0032] It has been shown that polar coagents are not useful for the present invention and they are excluded from the rubber compositions disclosed herein. These polar coagents typically increase both the rate and state of the cure and form very reactive radicals through addition reactions. Examples of these polar coagents include multifunctional acrylate and methacrylate esters and dimaleimides, such as the zinc salts of acrylic and methacrylic acid,

ethylene glycol diacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate and N, N'-m-phenylene dimaleimides.

[0033] The non-ionic coagents may be added to particular embodiments of the rubber compositions disclosed herein in an amount of between 1 phr and 7 phr or alternatively, between 2 phr and 6 phr or between 3 phr and 5 phr.

[0034] Other additives can be added to the rubber compositions disclosed herein as known in the art. Such additives may include, for example, some or all of the following: antidegradants, antioxidants, fatty acids, waxes, stearic acid and zinc oxide. Examples of antidegradants and antioxidants include 6PPD, 77PD, IPPD and TMQ and may be added to rubber compositions in an amount, for example, of from 0.5 phr and 5 phr. Zinc oxide may be added in an amount, for example, of between 1 phr and 6 phr or alternatively, of between 1.5 phr and 4 phr. Waxes may be added in an amount, for example, of between 1 phr and 5 phr.

[0035] The rubber compositions that are embodiments of the present invention may be produced in suitable mixers, in a manner known to those having ordinary skill in the art, typically using two successive preparation phases, a first phase of thermo-mechanical working at high temperature, followed by a second phase of mechanical working at lower temperature.

[0036] The first phase of thermo-mechanical working (sometimes referred to as "non-productive" phase) is intended to mix thoroughly, by kneading, the various ingredients of the composition, with the exception of the vulcanization system. It is carried out in a suitable kneading device, such as an internal mixer or an extruder, until, under the action of the mechanical working and the high shearing imposed on the mixture, a maximum temperature generally between 120° C and 190° C is reached.

[0037] After cooling of the mixture, a second phase of mechanical working is implemented at a lower temperature. Sometimes referred to as "productive" phase, this finishing phase consists of incorporating by mixing the vulcanization (or cross-linking) system, *i.e.*, the peroxide curing agent (coagents may be added in first phase), in a suitable device, for example an open mill. It is performed for an appropriate time (typically for

example between 1 and 30 minutes) and at a sufficiently low temperature lower than the vulcanization temperature of the mixture, so as to protect against premature vulcanization.

[0038] The rubber composition can be formed into useful articles, including treads for use on vehicle tires and in particular embodiments for tire treads for use on passenger cars and/or light trucks. The treads may be formed as tread bands and then later made a part of a tire or they be formed directly onto a tire carcass by, for example, extrusion and then cured in a mold. As such, tread bands may be cured before being disposed on a tire carcass or they may be cured after being disposed on the tire carcass. Typically a tire tread is cured in a known manner in a mold that molds the tread elements into the tread, including, *e.g.*, the grooves, ribs and/or blocks molded into the tread.

[0039] As is known to those skilled in the art, tires treads may be constructed in a layered form, such as a cap and base construction, wherein the cap is formed of one rubber composition and the base is formed in another rubber composition. It is recognized that in such tread constructions, the disclosed rubber compositions are useful for that part of the tread that actually makes contact with the running surface, *e.g.,* the road surface.

[0040] It should be noted that the foregoing included detailed references to particular embodiments of the present invention, which were provided by way of explanation of the invention. For example, features illustrated or described as part of one embodiment can be used with another embodiment to yield still a third embodiment. The invention is further illustrated by the following examples, which are to be regarded only as illustrations and not delimitative of the invention in any way. The properties of the compositions disclosed in the examples were evaluated as described below and these methods are suitable for measurement of the claimed properties of the present invention.

[0041] Modulus of elongation (MPa) was measured at 10% (MA10), 100% (MA100) and 300% (MA300) at a temperature of 23 °C based on ASTM Standard D412 on dumb bell test pieces. The measurements were taken in the second elongation; *i.e.*, after an accommodation cycle. These measurements are secant moduli in MPa, based on the original cross section of the test piece.

[0018] Dynamic properties (Tg and G*) for the rubber compositions were measured on a Metravib Model VA400 ViscoAnalyzer Test System in accordance with ASTM D5992-

96. The response of a sample of vulcanized material (double shear geometry with each of the two 10 mm diameter cylindrical samples being 2 mm thick) was recorded as it was being subjected to an alternating single sinusoidal shearing stress of a constant 0.7 MPa and at a frequency of 10 Hz over a temperature sweep from -60 °C to 100 °C with the temperature increasing at a rate of 1.5 °C/min. The shear modulus G* at 60 °C was captured and the temperature at which the max tan delta occurred was recorded as the glass transition temperature, Tg.

[0019] Near infrared (NIR) spectroscopy is used to quantitatively determine the weight content of styrene in the elastomer and also the elastomer microstructure (relative distribution of the 1,2-*vinyl*, *trans*-1,4- and *cis*-1,4-butadiene units). The principle of the method rests on the Beer-Lambert law applied to a multicomponent system. Since the method is indirect, it calls for a multivariate calibration [Vilmin, F.; Dussap, C.; Coste, N. Applied Spectroscopy 2006, 60, 619-29] carried out using standard elastomers having a composition determined by $_{13}C$ NMR. The styrene content and the microstructure are then calculated from the NW spectrum of an elastomer film of around 730 μm in thickness. The acquisition of the spectrum is carried out in transmission mode between 4000 and 6200 cm^{-1} with a resolution of 2 cm^{-1}, using a Bruker Tensor 37 Fourier transform NIR spectrometer equipped with a Peltier-cooled InGaAs detector.

[0020] The invention is further illustrated by the following examples, which are to be regarded only as illustrations and not delimitative of the invention in any way.

Example **1**

This example provides

[0042] Rubber compositions were prepared using the components shown in Table **1**. The amount of each component making up these rubber compositions are provided in parts per hundred parts of rubber by weight (phr). The polybutadiene was end-functionalized with silanol groups and had a vinyl-1.2 content of 13 wt%.

[0043] The resin was the C5-C9 resin Oppera 373N available from ExxonMobil and having a z average molecular weight greater than 20,000, a weight average molecular weight of about 2500, a softening point of about 89 °C and has a glass transition temperature of about

39 ° C. The antidegradants included wax and 6PPD. The BR contained 13 wt% *vinyl*-1,2 units, 51 wt% *trans*-1,4 units and 36 wt% *cis*-1,4 units.

Table **1** – Rubber Formulations

Formulations	**W1**	**F1**
f-BR	100	100
Carbon Black, N234	8.5	8.5
Silica	101	101
Si69	8.1	8.1
Resin	76.5	72.5
Antidegradants, Processing Aids, Activators	8.6	8.6
Sulfur	0.8	
CBS	1.75	
VULCUP R *		4
Physical Properties		
Shear Modulus G*60 @ 60 °C & 0.7 MPa	1.13	1.05
Tg, °C	-22.4	-26.4
MA10 @ 23 °C, MPa	4.8	4.4
MA100 @ 23 °C, MPa	1.6	1.1
MA300 @ 23 °C, MPa	1.7	1.0

*Peroxide component contained only 40% active peroxide

[0044] The peroxide curing agent was VULCUP R, which includes 60% non-active ingredients so that the amount of active peroxide was 1.6 phr of active peroxide for F**1**.

[0045] The rubber formulations were prepared by mixing the components given in Table **1**, except for the peroxide or sulfur and the coagents or accelerators, in a Banbury mixer by the process described above. The vulcanization package was added in the second phase on a mill. Vulcanization was effected (25 minutes at 170°C) and the formulations were then tested to measure their physical properties as reported in Table **1**.

[0021] The terms “comprising,” “including,” and “having,” as used in the claims and specification herein, shall be considered as indicating an open group that may include other elements not specified. The term “consisting essentially of,” as used in the claims and specification herein, shall be considered as indicating a partially open group that may include other elements not specified, so long as those other elements do not materially alter the basic and novel characteristics of the claimed invention. The terms “a,” “an,” and the singular forms of words shall be taken to include the plural form of the same words, such that the terms mean that one or more of something is provided. The terms “at least one” and “one or

more" are used interchangeably. The term "one" or "single" shall be used to indicate that one and only one of something is intended. Similarly, other specific integer values, such as "two," are used when a specific number of things is intended. The terms "preferably," "preferred," "prefer," "optionally," "may," and similar terms are used to indicate that an item, condition or step being referred to is an optional (not required) feature of the invention. Ranges that are described as being "between a and b" are inclusive of the values for "a" and "b."

[0022] It should be understood from the foregoing description that various modifications and changes may be made to the embodiments of the present invention without departing from its true spirit. The foregoing description is provided for the purpose of illustration only and should not be construed in a limiting sense. Only the language of the following claims should limit the scope of this invention.

CLAIMS

What is claimed is:

1. A tread for a tire, the tread comprising a rubber composition that is based upon a cross-linkable elastomer composition, the cross-linkable rubber composition comprising, per 100 parts by weight of rubber (phr):

between 80 phr and 100 phr of a polybutadiene-based elastomer modified with a functional group that is capable of interacting with a silica reinforcing filler, wherein a polybutadiene portion of the polybutadiene-based elastomer has between 8 wt% and 15 wt% vinyl units, wherein the polybutadiene-based elastomer includes at least 30 wt% *trans*-bonds and wherein the polybutadiene-based elastomer has a glass transition temperature of between -100° C and -80° C;

up to 20 phr of a second diene elastomer having a glass transition temperature of no greater than -80° C;

between 90 phr and 150 phr of a silica as the reinforcing filler;

an effective amount of a plasticizing system that includes a plasticizing resin having a glass transition temperature (Tg) of at least 25 °C, wherein the effective amount of the plasticizing system provides the rubber composition with a shear modulus G* measured at 60 °C of between 0.6 MPa and 1.5 MPa and a Tg of between -35° C and 0° C; and

a peroxide curing agent.

2. The tread of claim of 1, wherein the polybutadiene-based elastomer is a styrene-polybutadiene copolymer with no more than 4 wt% styrene based on the total weight of the styrene-polybutadiene copolymer.

3. The tread of claim 2, wherein the styrene-polybutadiene copolymer has no more than 3 wt% styrene.

4. The tread of claim 3, wherein the styrene-polybutadiene copolymer has between 0.5 wt% and 2 wt% styrene.

5. The tread of claim 1, wherein the polybutadiene-based elastomer is not a copolymer.

6. The tread of any of the preceding claims, wherein at least 80 wt% of the polybutadiene-based elastomer chains are functionalized.

7. The tread of any of the preceding claims, wherein the alkoxysilane functional group is capable of interacting with a reinforcing filler through an amino functional group of the alkoxysilane, the amino functional group being a primary, secondary or tertiary amino function.

8. The tread of claim 7, wherein the amino functional group is selected from diethylamine or dimethylamine.

9. The tread of any of the preceding claims, wherein the plasticizing system further comprises a plasticizing liquid.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/063021

A. CLASSIFICATION OF SUBJECT MATTER
INV. B60C1/00 C08C19/22 C08C19/25 C08K5/00 C08L9/00
C08L9/06
ADD. C08K3/36 C08K5/14
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)
B60C C08C C08K C08L

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2014/371346 A1 (SAINTIGNY XAVIER [US] ET AL) 18 December 2014 (2014-12-18) abstract paragraph [0021] - paragraph [0025] paragraph [0050] paragraph [0075]; claim 1; examples F1-F5; table 1 paragraph [0057] ----- -/--	1-9

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 July 2016	12/07/2016

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/063021

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/147827 A1 (MICHELIN RECH TECH [CH]; TECHNOLOGIES MICHELIN SOC D [FR]; CHEKANOV YU) 3 October 2013 (2013-10-03) abstract paragraph [0001] paragraph [0003] - paragraph [0005] paragraph [0006] paragraph [0042] paragraph [0055] - paragraph [0058]; claims 1,2; example F6; table 1 paragraph [0015] paragraph [0032]	1-9
A	WO 2014/179806 A1 (MICHELIN & CIE [FR]; MICHELIN RECH TECH [CH]; SAINTIGNY XAVIER [US]; P) 6 November 2014 (2014-11-06) paragraph [0001] paragraph [0008] paragraph [0048] - paragraph [0049] paragraph [0065] - paragraph [0067]	1-9
A	EP 2 412 731 A1 (GOODYEAR TIRE & RUBBER [US]) 1 February 2012 (2012-02-01) paragraph [0001] - paragraph [0002] paragraph [0004] claim 1; table 1	1-9
A	WO 2015/065884 A1 (MICHELIN & CIE [FR]; MICHELIN RECH TECH [CH]; CATO ANTHONY DERBIN [US]) 7 May 2015 (2015-05-07) paragraph [0001] paragraph [0004] - paragraph [0005] paragraph [0030] - paragraph [0031] paragraph [0060] - paragraph [0061] paragraph [0080] - paragraph [0082] tables 1, 2	1-9
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Information on patent family members

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PCT/US2015/063021

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