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(54) Title: ANISOTROPIC RUBBER COMPOSITION

(57) Abstract: Rubber compositions reinforced with an iron oxide reinforcement filler having anisotropic properties and articles formed therefrom. The anisotropic properties result from the iron oxide particles being directionally aligned within the matrix of the rubber composition. Such rubber composition include a highly unsaturated diene rubber resulting at least in part from conjugated diene monomers and having a content of such monomers that is greater than 50 mol%. The iron oxide particles may be aligned with the magnetic field lines from a magnet placed in proximity with the rubber composition.



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## ANISOTROPIC RUBBER COMPOSITION

### BACKGROUND OF THE INVENTION

#### Field of the Invention

[0001] This invention relates generally to rubber compositions and more particularly, to anisotropic rubber compositions having an iron oxide reinforcement filler.

#### Description of the Related Art

[0002] Rubber is a well-known polymer that is used in many products ranging from tires and other automobile applications to playground equipment, shoes, clothing, flooring and household supplies. Rubber comes in many forms and sources including, for example, natural production as from the rubber tree and synthetic production as from petrochemical sources.

[0003] Rubber is typically compounded with other materials in a rubber composition to provide the desired physical attributes of the cured rubber composition. Since rubber by itself is not particularly strong, reinforcement fillers may be added to improve its strength and, for example, to provide increased wear properties, rigidity and longevity for products made from the rubber compositions. Examples of well-known reinforcement fillers include carbon blacks and silica, both of which are extensively used in the tire industry to reinforce the rubber compositions that are used in tires. It is also known to use iron oxide as reinforcement filler in rubber compositions.

[0004] Research continues in the field of reinforcement fillers to improve the physical properties of the resulting rubber compositions and/or to improve the mixing, handling and processing of the rubber compositions that will be used to form useful products.

### SUMMARY OF THE INVENTION

[0005] Particular embodiments of the present invention include rubber compositions reinforced with an iron oxide reinforcement filler having anisotropic properties and articles formed therefrom. The anisotropic properties result from the iron oxide particles being directionally aligned within the matrix of the rubber composition. Such rubber composition include a highly unsaturated diene rubber resulting at least in part from conjugated diene

monomers and having a content of such monomers that is greater than 50 mol%. The iron oxide particles may be aligned with the magnetic field lines from a magnet placed in proximity with the rubber composition.

#### DETAILED DESCRIPTION OF PARTICULAR EMBODIMENTS

[0006] Particular embodiments of the present invention include rubber compositions and articles made from such rubber compositions including, for example, tires made at least in part from the rubber compositions disclosed herein. Surprisingly it has been found that very small particles, *i.e.*, of nanosized or approaching nanosized particles, of an iron oxide such as ferric oxide ( $\text{Fe}_2\text{O}_3$ ) can be useful in rubber composition as a rubber reinforcement filler and, when directionally aligned within the matrix of the rubber composition, the rubber composition becomes anisotropic. That is, such particles become aligned within the material and structure that is the matrix formed by the rubber composition. Advantageously the orientation of the iron oxide particles provides an anisotropic material with improved rigidity in the direction of their orientation but with little or no change in the hysteresis in a direction orthogonal to the orientation direction. The iron oxide particles can be aligned within the matrix of the rubber composition by directing the magnetic field of one or more magnetics in the direction of the desired alignment.

[0007] In particular embodiments, the disclosed rubber compositions are useful for the manufacture of rubber articles, which include tires and components that are found in tires. For example, particular embodiments may include tire treads or components found in the sidewall of a tire. Run-flat tires that are designed to run for a given distance while having no or very little inflation pressure include sidewall supports that help support the load when the tire is in a low or no inflation state. Such supports may be formed from the rubber compositions disclosed herein. Tire treads made from the disclosed rubber compositions may be included on passenger or light truck tires as well as, for example, on heavy truck, aircraft tires and agricultural tires. Other useful articles may include, for example, motor mounts, conveyer belts and hoses.

[0008] 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.

[0009] As used herein, elastomer and rubber are synonymous terms.

[0010] 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.

[0011] As is generally known, a tire tread includes 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 preferably being provided with a minimum amount of generated noise and at low rolling resistance.

[0012] Treads of the type disclosed herein include tread elements, 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 grooves that run in the substantially lateral (axial) direction or any other grooves that are oblique thereto. The radial (depth) direction is perpendicular to the lateral direction.

[0013] It is recognized that treads may be formed from only one rubber composition or in two or more layers of differing rubber compositions, *e.g.*, a cap and base construction. In a cap and base construction, the cap portion of the tread is made of one rubber composition that is designed for contact with the road. The cap is supported on the base portion of the tread, the base portion made of different rubber composition. In particular embodiments of the present invention the entire tread may be made from the rubber compositions disclosed herein while in other embodiments only the cap portions of the tread may be made from such rubber compositions or only the base may be made from such rubber compositions.

[0014] In other embodiments it is recognized that the contact surface of the tread elements, *i.e.*, that portion of the tread element that contacts the road, may be formed totally

and/or only partially from the rubber compositions disclosed herein. In particular embodiments the tread block, for example, may be formed as a composite of laterally layered rubber compositions such that at least one lateral layer of a tread block is of the rubber compositions disclosed herein and another lateral layer of a tread block is of an alternative rubber composition. For example, at least 80 % of the total contact surface area of the tread may be formed solely from the rubber compositions disclosed herein. The total contact surface area of the tread is the total surface area of all the radially outermost faces of the tread elements that are adapted for making contact with the road.

[0015] As noted above, embodiments of the rubber compositions disclosed herein include an iron oxide reinforcement filler. Iron oxides are well-known materials and are used in such industries as the iron industry in the production of alloys, in the polishing industry in the fine polishing of metallic jewelry and lenses, in the cosmetics industry, in the paint industry as a pigment and in the magnetic recording industry as a recording medium. Iron (II,III) oxide is also used in making the catalyst for the industrial synthesis of ammonia.

[0016] Large particles of iron oxide are not useful as a reinforcement filler in the disclosed rubber compositions. Therefore, particular embodiments of the rubber compositions disclosed herein include iron oxide particles having an average particle diameter capped at no more than 500 nm or alternatively, no more than 450 nm, no more than 400 nm, no more than 300 nm, no more than 250 nm, no more than 150 nm or no more than 100 nm. Particular embodiments of such rubber compositions may include a lower limit for each of these average diameter caps of 1 nm or alternatively 5 nm, 10 nm, 15 nm or 30 nm as the lower limit of a range of the average diameter of the iron oxide reinforcement filler. For example, the iron oxide may have an average diameter of between 5 nm and 150 nm or of between 30 nm and 150 nm. More particularly the iron oxide filler particles of particular embodiments may have an average particle diameter of between 5 nm and 500 nm or alternatively between 10 nm and 400 nm, between 15 nm and 300 nm, between 30 and 100 nm or between 30 nm and 65 nm.

[0017] Iron oxides are available in many forms. For example, ferrous oxide (FeO) is fairly rare and not readily available. The more common forms include iron (II, III) oxide (for example Fe<sub>3</sub>O<sub>4</sub>), which is naturally occurring as the mineral magnetite and iron (III) oxide

(Fe<sub>2</sub>O<sub>3</sub>), which is also known as ferric oxide and as the mineral hematite and is a source of iron for the steel industry.

[0018] In particular embodiments of the rubber compositions disclosed herein, the iron oxide reinforcement filler may be selected from the group consisting of ferric oxide, iron (II, III) oxide and combinations thereof. In other embodiments the iron oxide reinforcement filler may be just ferric oxide or alternatively, just iron (II,III) oxide. In particular embodiments, including those listed above, the iron (II,III) oxide may be limited to Fe<sub>3</sub>O<sub>4</sub>.

[0019] The amount of iron oxide reinforcement filler is determined by the degree of reinforcement desired in the resulting cured rubber composition and in those cases the amount of iron oxide is not particularly limited. In particular embodiments, however, the amount of iron oxide added to the rubber composition may be between 50 phr and 800 phr or alternatively between 50 phr and 500 phr, between 50 phr and 400 phr, between 100 phr and 800 phr, between 100 phr and 600, between 125 phr and 600 phr, between 125 phr and 800 phr, between 125 phr and 400 phr, between 200 phr and 500 phr, between 150 phr and 400 phr, between 200 phr and 300 phr or between 100 phr and 500 phr.

[0020] Iron oxides may be obtained from different sources. For example US Research Nanomaterials of Houston Texas provides iron oxides such as Fe<sub>2</sub>O<sub>3</sub> with an average particle size of 30 nm and in a different product, with an average particle size of between 20 nm and 40 nm. The also provide Fe<sub>3</sub>O<sub>4</sub> iron oxide with an average particle size of between 15 nm to 20 nm. Iron oxides are also available from Sigma-Aldrich with offices in St. Louis MO as ferric oxide with an average particle size less than 50 nm. Such particles provide reinforcement without first being coated with another material, such as silica. Therefore, particular embodiments of the rubber compositions disclosed herein may not be coated with silica or another material that provides a surface from which a linking agent can link it to the elastomer component.

[0021] Average particle size may be determined by several different methods as known to those skilled in the art including dynamic light scattering (DLS), microscopy (SEM or TEM) and calculating the particle size based on the BET surface area measurement. Methods that include the TEM determination and BET measurement provide suitable results.

[0022] For example, determination of the average particle diameter may be determined based on the following equation:  $d = 6000 / (\text{BET} * \text{Density})$ , wherein d is the average particle

diameter of the iron oxide in nanometers, BET is the BET surface area in  $\text{m}^2/\text{g}$  and density is the density of the particles in  $\text{g/cc}$ . An explanation of this test method may be found in the article A Case Study in Sizing Nanoparticles by F. Thiele, M. Poston and R. Brown and published by Micromeritics Analytical Services of Norcross GA, which article is hereby fully incorporated herein by reference. A suitable procedure for determining BET and density are provided below.

[0023] The BET measurement may be obtained in accordance with ASTM method D6556 to determine the nitrogen surface area SSA. For example, such measurements may be made on a TriStar II surface area and porosity instrument manufactured by Micromeritics. Samples may be treated with nitrogen gas to remove adsorbed contaminants, then cooled under vacuum using liquid nitrogen. Controlled increments of nitrogen gas are given to the sample at a constant temperature and a specified pressure. The gas volume adsorbed is calculated by the instrument software and the SSA (BET) is determined.

[0024] The density measurement may be obtained in accordance with ASTM C604-02 by gas comparison pycnometer. This technique uses the gas displacement method to measure volume accurately. For example, using a Micromeritics AccuPyc II 1340 pycnometer, an inert gas such as helium is used as the displacement medium. The sample is sealed in the instrument compartment of known volume, the helium is admitted, and then expanded into another precision internal volume. The pressures observed upon filling the sample chamber and then discharging it into a second empty chamber allow computation of the sample solid phase volume. Helium molecules rapidly fill pores as small as one angstrom in diameter; only the solid phase of the sample displaces the gas. Dividing this volume into the sample weight gives the gas displacement density.

[0025] It has been determined that iron oxide particles can be aligned within the matrix of the rubber composition by using magnetic force. When one or more magnets are placed adjacent to the rubber composition, the iron oxide particles align with the lines of magnetic field that the magnet produces, *i.e.*, the iron oxide particles align themselves end to end with the magnetic field lines. Surprisingly this occurs even with the iron oxide particles contained within the cross-linkable rubber composition.

[0026] To align the iron oxide particles, the magnet is placed in alignment with the rubber composition or article formed from the rubber composition so that the magnetic field lines

align with the desired alignment direction of the iron oxide particles. If more than one magnet is used, then the second magnet may be aligned on an opposite side of the rubber composition in a N-S pole arrangement. That is, the N pole of the first magnet is placed on a first side of the article and the N pole of the second magnet may be placed on a second side that is opposite the first side. The iron oxide particles will then align with the magnetic force produced between these two magnets. Typically the faces of the poles of the magnets will be essentially normal to one another or as close to normal as possible within the constraints of article shape, size and so forth.

[0027] To establish the desired magnetic field lines to which the iron oxide particles will align, the magnet(s) are placed over the alignment surfaces of the rubber composition/article. For example, if it is desired to align the iron oxide particles in the thickness direction of a disk, then a magnet pole face would be positioned to cover the top surface of the disk and optionally, another magnet would be positioned to cover the bottom surface of the disk. The iron oxide particles would then be aligned in the thickness direction between the alignment surfaces, *i.e.*, the top surface and the bottom surface of the disk. The alignment surface is the surface covered by the magnet pole face.

[0028] To achieve proper alignment, most of the alignment surface area should be covered by a pole face of the magnet. In other words, particular embodiments of the rubber composition disclosed herein provides that the pole face of the magnet cover at least 80% of the alignment surface area or alternatively at least 90%, at least 95% or at least 100% of the alignment surface area. "Covered" does not mean the magnet pole face must touch the alignment surface, only that the surface of the magnet pole face extend over the alignment surface with or without a gap therebetween.

[0029] Generally a magnet that generates stronger magnetic forces will provide better alignment of the iron oxide particles. Likewise magnets placed on opposite sides (or alignment surfaces) of the rubber composition or article will generate stronger magnetic forces to provide better particle alignment. Electromagnets can be designed to generate very powerful magnetic forces and are therefore useful magnets. Permanent magnets may also be used, especially rare earth magnets since they are known to be strong magnets. As is known, rare earth magnets are

made from alloys of the rare earth elements (elements in the lanthanide series plus scandium and yttrium).

[0030] In addition to trying to align the magnet pole faces as closely to normal as possible when placing two magnets to generate the magnetic field, it is also beneficial to place them as closely together as possible to exert the strongest magnetic alignment forces on the iron oxide particles.

[0031] Embodiments of the rubber compositions disclosed herein include a highly unsaturated diene rubber to which the iron oxide may be added and in which it may be aligned. Diene elastomers are known to be those elastomers resulting at least in part, *i.e.*, a homopolymer or a copolymer, from diene monomers, *i.e.*, monomers having two double carbon-carbon bonds, whether conjugated or not.

[0032] Generally diene elastomers may be classified as either “essentially unsaturated” diene elastomers or “essentially saturated” diene elastomers. As used herein, essentially unsaturated diene elastomers are diene elastomers resulting at least in part from conjugated diene monomers, the essentially unsaturated diene elastomers having a content of such members or units of diene origin (conjugated dienes) that is at least 15 mol. %. Within the category of essentially unsaturated diene elastomers are highly unsaturated diene elastomers, which are diene elastomers having a content of units of diene origin (conjugated diene) that is greater than 50 mol. %.

[0033] Those diene elastomers that do not fall into the definition of being essentially unsaturated are, therefore, the essentially saturated diene elastomers. Such elastomers include, for example, butyl rubbers and copolymers of dienes and of alpha-olefins of the EPDM type. These diene elastomers have low or very low content of units of diene origin (conjugated dienes), such content being less than 15 mol. %.

[0034] The elastomers useful in the rubber compositions disclosed herein may have any microstructure, such microstructure being a function of the polymerization conditions used, in particular of the presence or absence of a modifying and/or randomizing agent and the quantities of modifying and/or randomizing agent used. The elastomers may, for example, be block, random, sequential or micro-sequential elastomers, and may be prepared in dispersion or in

solution; they may be coupled and/or starred or alternatively functionalized with a coupling and/or starring or functionalizing agent.

[0035] Functionalized rubbers, *i.e.*, those appended with active moieties, are well known in the industry. The backbone or the branch ends of the elastomers may be functionalized by attaching these active moieties to the ends of the chains or to the backbone or mid-chains of the polymer. Exemplary functionalizing agents that could be included with the diene elastomers include, but are not limited to, metal halides, metalloid halides, alkoxysilanes, imine-containing compounds, esters, ester-carboxylate metal complexes, alkyl ester carboxylate metal complexes, aldehydes or ketones, amides, isocyanates, isothiocyanates and imines – all of these being well-known in the art. Particular embodiments may include functionalized diene elastomers while other embodiments may be limited to including no functionalized elastomers.

[0036] Examples of suitable highly unsaturated diene elastomers include, but are not necessarily limited to, polybutadienes (BR), polyisoprenes (IR), natural rubber (NR), butadiene copolymers, isoprene copolymers and mixtures of these elastomers. Such copolymers include butadiene/styrene copolymers (SBR), isoprene/butadiene copolymers (BIR), isoprene/styrene copolymers (SIR) and isoprene/butadiene/styrene copolymers (SBIR). Any of these examples or mixtures of these examples are suitable for particular embodiments of the rubber compositions disclosed herein.

[0037] Particular embodiments of the rubber compositions disclosed herein are limited to those having at least 80 phr of the rubber components being highly unsaturated diene elastomers. Other embodiments are limited to having at least 90 phr or 100 phr of the highly unsaturated diene elastomer components.

[0038] In addition to the highly unsaturated diene elastomers disclosed above or in lieu of such elastomers, epoxidized rubber components may also be useful rubber components. Such epoxidized rubber components result at least in part from conjugated diene monomers and typically having (in some embodiments required to have) a content of units of diene origin (conjugated diene) that is greater than 50 mol%. Such epoxidized rubber components may include, for example, an epoxidized polybutadiene rubber (eBR), an epoxidized styrene-butadiene rubber (eSBR), an epoxidized natural rubber (eNR), an epoxidized polyisoprene rubber (eIR), epoxidized butadiene copolymers, epoxidized isoprene copolymers and mixtures of

these elastomers including, for example, epoxidized isoprene/butadiene copolymers (eBIR), epoxidized isoprene/styrene copolymers (eSIR) and epoxidized isoprene/butadiene/styrene copolymers (eSBIR). The rubber compositions having an epoxidized rubber component may include, for example, any one of these epoxidized rubber components or combinations of any of them.

[0039] Particular embodiments may have the epoxidized rubber component selected from an epoxidized polybutadiene, an epoxidized natural rubber, an epoxidized polyisoprene rubber, an epoxidized styrene-butadiene rubber or combinations thereof. Alternatively the epoxidized rubber component may be limited to eBR, eSBR or combinations thereof. Alternatively the epoxidized rubber component may be limited to just eNR or alternatively just eNR, eSBR, eBR and combinations thereof.

[0040] Epoxidized rubber components are well-known in the art and may be obtained, as is known to those skilled in the art, by processes based on chlorohydrin or bromohydrin or processes based on hydrogen peroxides, alkyl hydroperoxides or peracids (such as peracetic acid or performic acid).

[0041] As noted above, not all of the epoxidized rubber components must be highly unsaturated rubber components, *i.e.*, having a content of conjugated diene origin that is greater than 50 mol%. While some embodiments only include highly unsaturated rubber components as the epoxidized rubber component, other embodiments may include rubber components having a content of conjugated diene origin that is at least 15 mol% but no more than 50 mol% (essentially unsaturated) or even less (essentially saturated diene elastomers). Examples of such epoxidized essentially saturated diene elastomers include an epoxidized butyl rubber (eIIR) and epoxidized copolymers of dienes and of alpha-olefins of the EPDM type (eEPDM). These are known to those skilled in the art and as examples, description of the epoxidation of eIIR is available in WO2014/089674 and a description of the epoxidation of eEPDM is available in EP0149192, both fully incorporated herein by reference for all that they disclose.

[0042] To obtain the targeted technical effect, the epoxidized rubber includes between 1 mol% and 25 mol% of the epoxy functionality or alternatively between 2 mol% and 25 mol%, between 2 mol% and 18 mol%, between 5 mol% and 25 mol%, between 5 mol% and 18 mol%, between 8 mol% and 15 mol%, between 3 mol% and 10 mol% or between 8 mol% and 20 mol%.

Since the T<sub>g</sub> of the rubber increases with increasing epoxy functionality, in particular embodiments greater than 25 mol% impacts the desired properties of the rubber compositions disclosed herein and less than the 1 mol% impacts the reactivity with the iron oxide reinforcement filler. The epoxy functionality by mole percent can be determined in known way through NMR analysis.

[0043] Typically, though not meant to be limiting of the invention, in those embodiments that include one of more epoxidized rubber components, diene rubber components that are not epoxidized may be limited to no more than 25 phr of such non-epoxidized diene rubber components. As is mentioned above, such diene elastomers are understood to be those elastomers resulting at least in part, *i.e.*, a homopolymer or a copolymer, from diene monomers, *i.e.*, monomers having two double carbon-carbon bonds, whether conjugated or not. Alternatively the rubber compositions disclosed herein may include the second rubber component in amounts that are capped at up to 20 phr, up to 10 phr or up to 5 phr. Particular embodiments of such rubber compositions may include a lower limit for each of these caps of 0 phr and others may include a lower limit of 5 phr; *e.g.*, between 0 phr and 25 phr or between 5 phr and 25 phr of such second rubber component. Examples of such diene elastomers were disclosed above and include such components as natural rubber, polybutadiene rubber, styrene-polybutadiene rubber and so forth.

[0044] It is noted that when the rubber compositions disclosed herein include an epoxidized rubber component, it is believed, though not limiting to the invention, that the iron oxide is useful as a reinforcement filler because it reacts or interacts with the epoxy function of the elastomer to reinforce it. In those embodiments that do not include at least 75 phr of epoxidized rubber component, then particular embodiments may further include two particular types of coupling agents that are useful for coupling the rubber components to the reinforcement filler.

[0045] Each of the coupling agents are bifunctional (meaning, unless otherwise indicated, at least bifunctional). More particularly, the rubber compositions include a first bifunctional coupling agent and a second bifunctional coupling agent, the first bifunctional coupling agent having an alkoxy silane as a first functional group and a moiety capable of bonding with the iron oxide as a second functional group. The second bifunctional coupling

agent also has an alkoxy silane as a third functional group and a moiety capable of bonding with the highly unsaturated diene elastomer as a fourth functional group.

[0046] Bonding as used herein includes any chemical bonding or interaction that is sufficient to establish an adequate connection necessary for reinforcing the rubber compositions, including covalent bonding, ionic bonding, hydrogen bonding, Van der Waals interactions and other interactions as may be known to those skilled in the art.

[0047] As is immediately apparent to those skilled in the art, the first bifunctional coupling agent includes a functional group capable of bonding the coupling agent to the iron oxide reinforcement filler. The second bifunctional coupling agent includes the moiety capable of bonding with the rubber, such coupling agents being well known as being useful as silica coupling agents in silica filled rubber compositions. Surprisingly, these two bifunctional coupling agents then bond between themselves through their alkoxysilyl functionalities, effectively creating a coupling agent for bonding the iron oxide reinforcement filler to the rubber component of the rubber composition.

[0048] Similarly to adding a silica coupling agent to a rubber composition when silica is added as a reinforcement filler, embodiments of the rubber compositions disclosed herein include adding the two bifunctional coupling agents to the rubber compositions when iron oxide is added as the reinforcement filler.

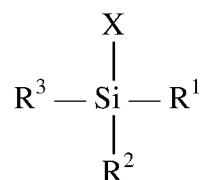
[0049] The first bifunctional coupling agent may be described with the simplified general formula "Z-T-Y", in which: Z represents a functional group ("Z" function) that is capable of bonding with the iron oxide, Y represents a functional group ("Y" function) that is capable of bonding with the second bifunctional coupling agent and T represents a divalent organic group making it possible to link Z and Y.

[0050] The second bifunctional coupling agent may be described with the simplified general formula "X-T'-Y'", in which: X represents a functional group ("X" function) that is capable of bonding with the diene elastomer, Y' represents a functional group ("Y'" function) that is capable of bonding with the first bifunctional coupling agent and T' represents a divalent organic group making it possible to link X and Y'.

[0051] It may be noted that T and T' are not particularly limited but a propyl alkyl group is often utilized since that 3-carbon chain length is recognized as being advantageous as

the length separating the X and Y' and Z and Y functionalities in particular embodiments. However, in some embodiments T and/or T' may be null with zero carbon atoms, with the X and Y' or the Z and Y functionalities bonded directly together without the divalent organic group. In particular embodiments the divalent organic group may include between zero and 10 carbon atoms or alternatively between 1 and 5 carbon atoms. Such groups may be an alkyl chain.

[0052] For the rubber compositions disclosed herein, the functional groups that interact with one another (Y and Y') may be the same or different but they must include an alkoxysilyl functionality, that is the silica atom must have at least one alkyl group bonded to it through an oxygen atom, *i.e.*, Si — O — R, wherein R is an alkyl group. The alkoxysilyl functionality may be represented as the following structural formula bonded to X:

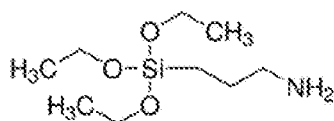


wherein R<sup>1</sup> is OR', wherein R' may in some embodiments be an alkyl group consisting of between 1 and 8 carbons or alternatively between 1 and 5 or between 1 and 3 carbons atoms and wherein R<sup>2</sup> and R<sup>3</sup> are the same or different and are selected from being OR' as the same or different from R<sup>1</sup>, an OH, an H or in some embodiments an alkyl group consisting of between 1 and 8 carbons or alternatively between 1 and 5 or between 1 and 3 carbons atoms and X is either the organic divalent group T or, if the functional groups of the bifunctional coupling agent are linked directly together, then X is the other such functional group. In particular embodiments the alkoxysilyl R' is limited to being an unbranched alkyl chain but in other embodiments, R' may include a branched alkyl chain, substituted or not.

[0053] Some embodiments of the rubber compositions disclosed herein may be limited to having coupling agents that have at least bialkoxysilyl functionalities and others may be limited to having coupling agents that have only trialkoxysilyl functionalities.

[0054] In addition to the alkoxysilyl functionality, the first bifunctional coupling agent further includes the functionality capable of bonding with the iron oxide reinforcement filler, the Z functionality. Such functionalities include chelating agents that will bond with the iron oxide.

Such chelating agents include amines and substituted amines. One example of a suitable first bifunctional coupling agent is (3-aminopropyl)triethoxysilane (APTES), which is also known as 3-triethoxysilylpropylamine, which is:



[0055] Other examples, all of which are available from Gelest, Inc. with offices in Morrisville, PA, include 4-aminobutyltriethoxysilane, 3-aminopropyl-trimethoxysilane, 3-aminopropylmethyldiethoxysilane, N-(2-aminoethyl)-3-aminopropyltri-methoxysilane, n-butylaminopropyltrimethoxysilane, (3-trimethoxysilylpropyl)diethylenetriamine, N,N'-bis[(3-trimethoxysilyl)propyl]ethylenediamine, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, (aminoethylaminomethyl)phenethyltrimethoxysilane, N,N'-bis[3-(triethoxysilyl)propyl]urea, and N,N'-bis[3-(trimethoxysilyl)propyl]urea.

[0056] In addition to the alkoxysilyl functionality, the second bifunctional coupling agent further includes the functionality capable of bonding with the diene elastomer, the X functionality. Such coupling agents are very well known in the rubber industry since such coupling agents are used as silane coupling agents – those coupling agents having the alkoxysilyl functionality for bonding to the silica and the X functionality for bonding to the diene elastomer. As is known in the art, the X functionality is often a sulfur or alternatively may be, for example, an epoxy group, a vinyl group or a methacryloxy group, all well-known examples of alternatives to using sulfur as the X functionality.

[0057] Examples of coupling agents that would be suitable as the second bifunctional coupling agent include the well-known coupling agents 3,3'-bis(triethoxysilylpropyl)disulfide (TESPD) and 3,3'-bis(triethoxysilylpropyl)tetrasulfide (TESPT) having disulfide or tetrasulfide functionalities respectively for bonding to the diene elastomer. Other examples 2,2'-bis(triethoxysilylethyl)tetrasulfide, 3,3'-bis(tri-t-butoxysilyl-propyl)disulfide and 3,3'-bis(di t-butyl methoxysilylpropyl)tetrasulfide, 2-mercaptoethyl-trimethoxysilane, 3-mercaptopropylmethyldimethoxysilane and 2-mercaptodimethylmethoxy-silane. Examples of those having a different functionality than sulfur for bonding to the diene rubber include those with epoxy functionality such as 3-Glycidoxypropyl methyldimethoxy silane, 3-Glycidoxypropyl

trimethoxysilane, those with vinyl functionalities such as vinyltrimethoxysilane and vinyltriethoxysilane and those with methacryoxy functionalities such as 3-methacryloxypropyl methyldimethoxysilane and 3-methacryloxypropyl trimethoxysilane. All of these are well-known and are available, for example, from Shin-Etsu Chemical Co, Ltd. Of Tokyo, Japan. Note that in the examples of the vinyl functionalities the T divalent organic group is not included. As noted, some embodiments of the rubber compositions disclosed herein include bifunctional coupling agents wherein the T divalent organic group is missing or alternatively, is optional.

[0058] The two bifunctional coupling agents are added in an amount proportional to the amount of iron oxide added to the rubber composition. The amount of bifunctional coupling agent can vary over a suitable range as known to one having ordinary skill in the art. Typically the amount total of the two bifunctional coupling agents added is between 1 wt. % and 15 wt. % or alternatively between 2 wt. % and 10 wt. % or between 3 wt. % and 7 wt. % of the total weight of iron oxide added to the rubber composition. The split between the two coupling agents may, in particular embodiments, be equal moles of each since one mole of the first bifunctional will react with one mole of the second bifunctional coupling agent. As is recognized by those skilled in the art it may in some applications be necessary to have an excess of one of the coupling agents over the other to drive the desired bonding.

[0059] In addition to the rubber components, the iron oxide particles and if needed, the two bifunctional coupling agents, particular embodiments may further include an amount of a secondary reinforcement filler, such as carbon black, silica or combinations thereof as is well-known in the industry. Particular embodiments include only the iron oxide reinforcement filler with no secondary reinforcement fillers.

[0060] If a secondary reinforcement filler is included in the rubber composition, determining the amount that may be added is within the knowledge of one skilled in the art. Such amounts are not particularly limited since the amounts will be determined in known way by those skilled in the art to provide the desired properties. Particular embodiments of the rubber compositions disclosed herein are limited to including no other reinforcement filler other than the iron oxide or alternatively, no more than up to 10 phr or alternatively no more than up to 5 phr of carbon black as necessary to provide black color to the rubber composition or as a carrier for the bifunctional coupling agent. Other embodiments may include just carbon black as a

secondary reinforcement filler, just silica as a secondary reinforcement filler or combinations thereof. Of course as is known, if silica is added as a secondary filler, sufficient silane coupling agent is required in the rubber composition to create bonds between the silica filler and the diene rubber. Therefore in particular embodiments the reinforcement filler is limited to no silica.

[0061] In addition to the highly unsaturated rubber component, the iron oxide reinforcement filler and the secondary reinforcement filler, particular embodiments may further include a plasticizing system. Plasticizing systems are well known in the art and are used for adjusting the processability of the rubber composition as well as adjusting the final cured properties of the rubber composition including the glass transition temperature (T<sub>g</sub>).

[0062] For example, a plasticizing system is described in patent application publication WO2016/106408 that is useful for rubber compositions, including those having a functionalized rubber component, such publication being hereby fully incorporated by reference for all that it teaches.

[0063] Suitable plasticizing systems may include, for example, high T<sub>g</sub> resins (T<sub>g</sub> greater than 23° C), low T<sub>g</sub> resins and/or liquid plasticizers such as oil. Although any of the known resins may be useful for particular embodiments, and the rubber compositions disclosed herein are not particularly limited to any one plasticizing system, terpene-phenol resins and hydrocarbon resins derived from petroleum products are useful examples of a suitable high T<sub>g</sub> resin.

[0064] Terpene phenolic resins are available on the market from, for example, Arizona Chemical having offices in Savannah, GA. Arizona Chemical markets a range of terpene phenolic resins under the name SYLVARES with varying softening points (SP), glass transition temperatures (T<sub>g</sub>) hydroxyl numbers (HN), number-average molecular masses (M<sub>n</sub>) and polydispersity indices (Ip), examples of which include: SYLVARES TP105 (SP: 105 °C; T<sub>g</sub>: 55 °C; HN: 40; M<sub>n</sub>: 540; Ip:1.5); SYLVARES TP115 (SP: 115 °C; T<sub>g</sub>: 55 °C; HN: 50; M<sub>n</sub>: 530; Ip:1.3); and SYLVARES TP2040 (SP: 125 °C; T<sub>g</sub>: 80 °C; HN: 135-150; M<sub>n</sub>: 600; Ip:1.3).

[0065] Other useful resins include the OPPERA resins available from ExxonMobil, these resins being modified aliphatic hydrocarbon resins, and SYLVARES 600 resin (M<sub>n</sub> 850 g/mol; Ip 1.4; T<sub>g</sub> 47° C.; HN of 31 mg KOH/g) that is an octyl phenol-modified copolymer of styrene and alpha methyl styrene as well as the coumarone-indene resins.

[0066] It may be noted that the glass transition temperatures of plasticizing resins may be measured by Differential Scanning Calorimetry (DCS) in accordance with ASTM D3418 (1999).

[0067] As noted, if the Tg of the rubber composition is too high with the addition of the high Tg resin, then the Tg can be adjusted downward by adding a plasticizing oil or a low Tg resin. 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.

[0068] 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 a suitable plasticizing oil is limited to a vegetable oil having a high oleic acid content.

[0069] The amounts of high Tg resin, low Tg resin and liquid plasticizer useful in any particular embodiment depends upon the particular circumstances and the desired results. Some embodiments may include no plasticizing system at all. Others may include just a high Tg resin or just a plasticizing oil. Such determinations are well within the skill of those having ordinary skill in the art. Examples of useful amounts of plasticizing oil for some embodiments may be zero or alternatively between 0 or 10 phr and 60 phr or alternatively, between 0 or 10 phr and 55 phr, between 0 or 10 phr and 50 phr, between 0 or 5 phr and 40 phr or between 0 or 10 phr and 35 phr. Examples of useful amounts of high Tg resin for some embodiments may be zero or alternatively between 0 phr and 150 phr, between 5 phr and 150 phr or between 10 phr and 100 phr of the high Tg resin.

[0070] The rubber compositions disclosed herein may be cured with any suitable curing system including a peroxide curing system or a sulfur curing system. Particular embodiments are cured with a sulfur curing system that includes free sulfur and may further include, for example, one or more of accelerators, stearic acid and zinc oxide. Suitable free sulfur includes, for example, pulverized sulfur, rubber maker's sulfur, commercial sulfur, and insoluble sulfur. The amount of free sulfur included in the rubber composition is not limited and may range, for example, between 0.5 phr and 10 phr or alternatively between 0.5 phr and 5 phr or between 0.5 phr and 3 phr. Particular embodiments may include no free sulfur added in the curing system but instead include sulfur donors.

[0071] Accelerators are used to control the time and/or temperature required for vulcanization and to improve the properties of the cured rubber composition. Particular embodiments of the present invention include one or more accelerators. One example of a suitable primary accelerator useful in the present invention is a sulfenamide. Examples of suitable sulfenamide accelerators include n-cyclohexyl -2-benzothiazole sulfenamide (CBS), N-tert-butyl-2-benzothiazole Sulfenamide (TBBS), N-Oxydiethyl-2-benzthiazolsulfenamid (MBS) and N'-dicyclohexyl-2-benzothiazolesulfenamide (DCBS). Combinations of accelerators are often useful to improve the properties of the cured rubber composition and the particular embodiments include the addition of secondary accelerators.

[0072] Particular embodiments may include as a secondary accelerant the use of a moderately fast accelerator such as, for example, diphenylguanidine (DPG), triphenyl guanidine (TPG), diorthotolyl guanidine (DOTG), o-tolylbigaunide (OTBG) or hexamethylene tetramine (HMTA). Such accelerators may be added in an amount of up to 4 phr, between 0.5 and 3 phr, between 0.5 and 2.5 phr or between 1 and 2 phr. Particular embodiments may exclude the use of fast accelerators and/or ultra-fast accelerators such as, for example, the fast accelerators: disulfides and benzothiazoles; and the ultra-accelerators: thiurams, xanthates, dithiocarbamates and dithiophosphates.

[0073] 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.

[0074] 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.

[0075] 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, more narrowly between 130° C and 170° C, is reached.

[0076] 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 (sulfur or other vulcanizing agent and accelerator(s)), in a suitable device, for example an open mill. It is performed for an appropriate time (typically between 1 and 30 minutes, for example between 2 and 10 minutes) and at a sufficiently low temperature lower than the vulcanization temperature of the mixture, so as to protect against premature vulcanization.

[0077] Particular embodiments of a useful method include mixing the ingredients of the rubber composition in a first phase, the ingredients being those included in the rubber compositions disclosed and/or claimed herein; mixing the curing agent, such as sulfur, into the rubber composition in a second phase. Particular embodiments may further include forming an article from the rubber composition and subjecting the article to a magnetic field. The method may further include curing the article.

[0078] Between the first phase of mixing and the second phase of mixing, particular embodiments of such methods may include cooling the mixture to a temperature below the curing temperature, for example by transferring the mixture to a mill and cooling the mixture on the mill.

[0079] Subjecting the article to a magnetic field may further include placing one or more magnets adjacent to the article; selecting a desired direction of alignment; aligning the one or more magnets with the article in the desired direction of alignment. Particular embodiments may include placing one or more magnets on opposite sides of the article. Such methods may further include aligning the faces of the opposing magnets essentially normal to each other; and aligning similar poles to the opposing sides of the article.

[0080] The rubber composition can be formed into useful articles, including treads for use on vehicle tires. 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 sipes molded into the tread blocks.

[0081] To align the iron oxide particles within the rubber composition, particular embodiments include placing the rubber composition (or article formed from the rubber composition) within the magnetic field so that the iron oxide particles can align in the desired direction. The alignment surface(s) is therefore placed within the magnetic field so that the magnet pole covers the alignment surface(s). The magnetic field may be applied before the article is cured, while the article is being cured or both.

[0082] 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 utilized methods are suitable for measurement of the claimed properties of the claimed invention.

[0083] Modulus of elongation (MPa) was measured at 10% (MA10), 100% (MA100) and 300% (MA300) at a temperature of 23 °C based on samples taken from the cured disks. The measurements were taken in the second elongation; *i.e.*, after an accommodation cycle.

[0084] The elongation property was measured as elongation at break (%) and the corresponding elongation stress (MPa), which is measured at 23 °C in accordance with ASTM Standard D412 on ASTM C test pieces.

[0085] The maximum tan delta dynamic properties for the rubber compositions were measured at 23° C 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 at a frequency of 10 Hz under a controlled temperature of 23° C. Scanning was effected at an amplitude of deformation of 0.05 to 50 % (outward cycle) and then of 50 % to 0.05% (return cycle). The maximum value of the tangent of the loss angle tan delta (max tan  $\delta$ ) was determined during the return cycle.

#### Example 1

[0086] A rubber composition was prepared using the components shown in Table 1. The amount of each component making up the rubber compositions are provided in parts per hundred parts of rubber by weight (phr).

Table 1 – Rubber Formulations

| Formulations | F1   |
|--------------|------|
| BR           | 100  |
| Resin        | 73   |
| Ferric Oxide | 265  |
| Si69         | 5.23 |
| Wax          | 1.5  |
| 6PPD         | 2    |
| DPG          | 0.9  |
| Cure Package | 8.9  |

[0087] The resin was Oppera 373N available from ExxonMobil and having a z-average molecular weight greater than 20,000, a weight average molecular weight of about 2500 Da, a softening point of about 89 ° C and a glass transition temperature of about 39 ° C. The iron oxide was ferric oxide and was obtained from Sigma Aldrich. and had an average particle diameter of less than 50 nm. The cure package included sulfur and accelerators as well as zinc oxide and stearic acid. Note that the rubber composition does not include both coupling agents but only Si69. If APTES had also been added as a coupling agent, the rigidity would have been higher as a result of improved coupling between the rubber and the iron oxide.

[0088] The rubber formulations were prepared by mixing the components given in Table 1, except for the accelerators and sulfur, in a Banbury mixer until a temperature of

between 110 °C and 170 °C was reached. The accelerators and sulfur were added in the second phase on a mill. The rubber was finally milled to a milled sheet that was about 5 mm thick.

#### Example 2

[0089] This example demonstrates how the iron oxide particles in the rubber composition of Example 1 were aligned. About 4 or 5 disks were cut by hand from the milled sheets produced in Example 1. The diameter of the disks was about 75 mm. The disks were placed in a mold and cured as a disk at a temperature of 150 ° C for one hour at greater than 4000 foot pounds. Prior to curing and during curing the disks were subjected to a magnetic field produced from two magnets, one placed above top surface of the disk and the other placed below the bottom surface of the disk inside of the mold. This would orient the iron oxide particles in the lateral direction, *i.e.*, in the thickness direction.

[0090] The magnets were neodymium disc magnets that were 3 inches in diameter and 0.25 inches thick and were obtained from McMaster-Carr. The magnets had a 50 pound pull, the amount of force required to pull the magnet from a rust-free, non-painted iron plate.

Table 2 – Properties

| Physical Properties    | radial | Z    | % Increase |
|------------------------|--------|------|------------|
| Modulus 10%, MPa       | 2.82   | 3.23 | 15         |
| Modulus 25%, MPa       | 2.35   | 2.81 | 20         |
| Modulus 50%, MPa       | 2.14   | 2.6  | 21         |
| Modulus 100%, MPa      | 2.23   | 2.75 | 23         |
| Modulus 200%, MPa      | 3.07   | 3.87 | 26         |
| Modulus 300%, MPa      | 3.22   | 4.03 | 25         |
| 300/100                | 1.44   | 1.47 | -          |
| Elongation at Break, % | 905    | 650  | -28        |
| Break Force, MPa       | 15.8   | 13.1 | -17        |
| Max tan delta at 23 °C | 0.22   | 0.23 | -          |

[0091] Samples were cut from the cured disks, both in the radial direction and in the lateral (z) direction to determine the anisotropic character of the cured rubber composition. The results are shown in Table 2.

[0092] As shown in Table 2, the rigidity in the z-dimension was significantly higher than that in the radial direction showing the anisotropic characteristic of the rubber composition.

There was also a significant change in the elongation properties in the different directions but basically no change in the hysteresis property of the rubber composition.

[0093] 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.”

[0094] 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 rubber composition that is based upon a cross-linkable rubber composition, the cross-linkable rubber composition comprising, in parts by weight per 100 parts by weight of rubber (phr):

a highly unsaturated diene rubber resulting at least in part from conjugated diene monomers and having a content of such monomers that is greater than 50 mol%;

iron oxide particles having an average particle diameter of no more than 500 nm, wherein the iron oxide particles create an anisotropic mechanical property in the rubber composition.

2. The rubber composition of claim 1, wherein the iron oxide particles create the anisotropic mechanical property by being directionally aligned within a matrix of the rubber composition.

3. The rubber composition of claim 1 or 2, wherein the anisotropic mechanical property is a rigidity property, an elongation property or both.

4. The rubber composition of any of the preceding claims, wherein the iron oxide particles are selected from the group consisting of ferric oxide, iron (II, III) oxide and combinations thereof.

5. The rubber composition of claim 4, wherein the iron oxide reinforcement filler is ferric oxide.

6. The rubber composition of claim 4, wherein the iron (II, III) oxide is  $\text{Fe}_3\text{O}_4$ .

7. The rubber composition of any of the preceding claims, wherein the iron oxide reinforcement filler has an average particle diameter of no more than 250 nm.

8. The rubber composition of claim 7, wherein the iron oxide reinforcement filler has an average particle diameter of no more than 100 nm.
9. The rubber composition of claim 7, wherein the iron oxide reinforcement filler has an average particle diameter of between 30 nm and 65 nm.
10. The rubber composition of any of the preceding claims, wherein the cross-linkable rubber composition comprises between 50 phr and 800 phr of the iron oxide reinforcing filler.
11. The rubber composition of claim 10, wherein the cross-linkable rubber composition comprises between 125 phr and 600 phr of the iron oxide reinforcing filler.
12. The rubber composition of claim 10, wherein the cross-linkable rubber composition comprises between 150 phr and 400 phr of the iron oxide reinforcing filler.
13. The rubber composition of any of the preceding claims, where the cross-linkable rubber composition further comprises a secondary reinforcement filler selected from the group consisting of carbon black, silica and combinations thereof.
14. The rubber composition of any of the preceding claims, wherein the highly unsaturated diene elastomer comprises at least 75 phr of an epoxidized rubber component.
15. The rubber composition of claim 14, wherein the epoxidized rubber component is selected from the group consisting of an epoxidized polybutadiene, an epoxidized natural rubber, an epoxidized polyisoprene rubber, an epoxidized styrene-butadiene rubber and combinations thereof.
16. The rubber composition of any of claims 1 through 13, wherein the highly unsaturated diene elastomer comprises at least 75 phr of one selected from the group consisting of a polybutadiene, a polyisoprene, a natural rubber, a butadiene copolymer, an isoprene copolymer and mixtures thereof.

17. An article formed at least in part from the rubber composition of any of the preceding claims.

18. The article of claim 17, wherein the article is a tire comprising a tread, an undertread or both wherein the tread, the undertread or both are formed from the rubber composition.

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2017/067178

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C08K3/22 C08J5/00  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08K C08J

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. |
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Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents :

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

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"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

16 March 2018

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2017/067178

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                | Relevant to claim No. |
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Information on patent family members

International application No

PCT/US2017/067178

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