Abstract:

A tire tread comprising a rubber composition that is based upon a cross-linkable elastomer composition, the cross-linkable elastomer composition comprising, per 100 parts by weight of rubber (phr) a highly unsaturated rubber and greater than 45 phr of a terpene phenolic resin. The rubber composition may further include a reinforcing filler and a curing system. Optionally the highly unsaturated rubber may be functionalized with an end-chain silanol group and in some embodiments, the entire rubber component of the rubber composition may be such a functionalized rubber, e.g., a silanol end-chain functionalized SBR.
RUBBER COMPOSITION WITH RESINS

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] This invention relates generally to rubber compositions useful for rubber articles and more particularly, to rubber compositions containing hydrocarbon resins.

Description of the Related Art

[0002] It is known in the industry that tire designers must often 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 increased traction of the tire and the Mooney viscosity of the unvulcanized mix. Tire traction can be improved by increasing the amount of filler in the tire but, with the addition of more filler, the Mooney viscosity increases, making the processing of the mix more difficult.

[0003] Tire designers and those conducting research in the tire industry continue to search for materials and tire structures that can break some of the known compromises. It would be desirable to break the known compromise between tire traction and Mooney viscosity of the unvulcanized mix.

SUMMARY OF THE DISCLOSURE

[0004] Particular embodiments of the present invention include a tire tread comprising a rubber composition that is based upon a cross-linkable elastomer composition, the cross-linkable elastomer composition comprising, per 100 parts by weight of rubber (phr) a highly unsaturated rubber and greater than 45 phr of a terpene phenolic resin. The rubber composition may further include a reinforcing filler and a curing system.

Optionally the highly unsaturated rubber may include a functionalized rubber with an end-chain silanol group and in some embodiments, the entire rubber content of the rubber composition may be such a functionalized rubber, e.g., a silanol end-chain functionalized SBR.
the entire rubber component of the rubber composition may exist of such functionalized rubber such as, in some embodiments, SBR.

It is recognized that for some embodiments of the cross-linkable rubber composition the terpene phenolic resin has a hydroxyl content of between 50 mg KOH/g and 200 mg KOH/g and further may include between 50 phr and 150 phr of the reinforcing filler.

The foregoing and other objects, features and advantages of the invention will be apparent from the following more detailed descriptions of particular embodiments of the invention.

DETAILED DESCRIPTION OF PARTICULAR EMBODIMENTS

Particular embodiments of the present invention include tires, other articles that include rubber at least in part and methods for their making. It has been found that when tire treads are made from rubber compositions disclosed herein, the compromise between traction and Mooney viscosity of the unvulcanized mix may be broken. Embodiments of such rubber compositions include a terpene phenolic resin and may optionally include elastomers that are functionalized.

As used herein, "phr" or "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.

As used herein, elastomer and rubber are synonymous terms.

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 or comprises the constituents of the cross-linkable rubber composition.

Reference will now be made in detail to embodiments of the invention. Each example is 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. It is intended that the present invention include these and other modifications and variations.

[0013] 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 with a low rolling resistance.

[0014] Treads of the type disclosed have, in particular embodiments, tread elements that are the structural features of the tread that contract the ground. Such structural features may be of any type of 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.

[0015] As noted above, particular embodiments of the present invention include treads for tires and other articles made at least in part of rubber compositions that include terpene phenolic resins. Terpene phenolic resins are well known materials that are often used as tackifiers. When used as tackifiers these resins are added in small quantities to increase the tackiness of the material and thereby aid in manufacturing as known to those skilled in the art. They are known to possess high polarity and high softening points and are known to be particularly useful in hot melt adhesive formulations. It is the addition of these high polarity resins that have surprisingly been found to break the compromise between the Mooney viscosity of the rubber composition and the traction of tire treads that include these resins.

[0016] Terpene phenolic resins are produced by the copolymerization of terpene monomers and phenol. As is known, terpene monomers include alpha-pinene, beta-pinene and limonene monomers, with the limonene monomers existing in three possible isomers: L-limonene (laevorotatory enantiomer), D limonene (dextrorotatory enantiomer) or else dipentene, the racemate of the dextrorotatory and laevorotatory enantiomers. Useful terpene phenolic resins may be those that include the copolymerization of the monomers selected
from alpha-pinene, beta-pinene, limonene monomers or combinations thereof with phenol. These types of resins are sometimes known as phenol modified terpene resins.

[0017] The degree of polarity of the terpene phenolic resins is determined by the number of hydroxyl groups contained within the resin. The higher the hydroxyl content, the greater the polarity of the terpene phenolic resin. The hydroxyl number of the resin is the amount, in milligrams, of potassium hydroxide equivalent to the hydroxyl groups in a 1 g sample of the resin and is, therefore, a measure of the concentration of hydroxyl groups in the resin. It is determined in known manner in accordance with ASTM E222.

[0018] It has been found that those terpene phenolic resins having at least a minimum hydroxyl number are useful for improving the traction of the rubber composition that contain them in accordance with the rubber compositions disclosed herein. Thus the useful terpene phenolic resins in particular embodiments have a hydroxyl number of at least 50 mg KOH/g or alternatively at least 55 mg KOH/g or at least 60 mg KOH/g. In other embodiments, the maximum hydroxyl number may be limited no more than 200 mg KOH/g or alternatively no more than 175 mg KOH/g or no more than 150 mg KOH/g. Other embodiments may include terpene phenolic resins having a range of between any one of the above-stated minimums above and any one of the above-stated maximums, such as between 50 mg KOH/g and 200 mg KOH/g, between 50 mg KOH/g and 175 mg KOH/g or between 60 mg KOH/g and mg KOH/g.

[0019] Additionally, particular embodiments of the rubber composition disclosed herein include a terpene phenolic resin that exhibits at least any one or any combination of the following characteristics: a glass transition temperature (Tg) of above 25 °C or alternatively above 35 °C, between 30 °C and 100 °C or between 30 °C and 95 °C; a softening point above 50 °C or alternatively between 50 °C and 150 °C; a number-average molar mass (Mn) of between 400 g/mol and 2000 g/mol or alternatively between 500 g/mol and 1500 g/mol or between 500 g/mol and 700 g/mol; a polydispersity index (Ip) of less than 3 or alternatively less than 2, wherein the polydispersity index is the weight average molecular mass (Mw) divided by Mn.

[0020] As used herein, the softening point is determined by the "Ring and Ball" method such as described in ASTM E-28. The glass transition temperatures may be measured
by Differential Scanning Calorimetry (DSC) in accordance with ASTM D3418 (1999). The macrostructure (Mw, Mn and Ip) of the resins are determined by size exclusion chromatography (SEC) which consists, for example, of separating the macromolecules in solution according to their size through columns filled with a porous gel. The molecules are separated according to their hydrodynamic volume, the bulkiest being eluted first. The sample to be analyzed is simply dissolved beforehand in an appropriate solvent, tetrahydrofuran at a concentration of 1 g/liter. The solution is then filtered through a filter with a porosity of 0.45 microliters before injection into the apparatus. The apparatus used is, for example, a "Waters Alliance" chromatographic line according to the following conditions: elution solvent: tetrahydrofuran; temperature: 35 °C; concentration: 1 g/litre; flow rate: 1 ml/min; injected volume: 100 microliters; Moore calibration with polystyrene standards; set of 3 "Waters" columns in series ("Styragel HR4E", "Styragel HR1" and "Styragel HR 0.5"); detection by differential refractometer (for example "WATERS 2410") which may be equipped with operating software (for example "Waters Millenium.").

[0021] A Moore calibration is carried out with a series of commercial polystyrene standards having a low Ip (less than 1.2), with known molar masses, covering the range of masses to be analyzed. The weight-average molar mass (Mw), the number-average molar mass (Mn) and the polydispersity index (Ip=Mw/Mn) are deduced from the data recorded.

[0022] 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 (Tg) hydroxyl numbers (HN), number-average molecular masses (Mn) and polydispersity indices (Ip), examples of which include: SYLVARES TP105 (SP: 105 °C; Tg: 55 °C; HN: 40; Mn: 540; Ip:1.5); SYLVARES TP115 (SP: 115 °C; Tg: 55 °C; HN: 50; Mn: 530; Ip:1.3); and SYLVARES TP2040 (SP: 125 °C; Tg: 80 °C; HN: 135-150; Mn: 600; Ip:1.3).

[0023] The rubber compositions disclosed herein include the terpene phenolic resin in amounts that are greater than the amount typically used as a tackifier, which is about 1 phr to 5 phr. Particular embodiments of the rubber compositions disclosed herein include the terpene phenolic resin in an amount that is greater than 45 phr or alternatively at least 55 phr.
or at least 65 phr of the terpene phenolic resin. In other embodiments, the maximum amount of the terpene phenolic resin may be limited to be no more than 120 phr of the terpene phenolic resin or alternatively, no more than 110 phr or no more than 90 phr of the resin. Other embodiments may include the amount of the terpene phenolic resins having a range of between any one of the above-stated minimums and any one of the above-stated maximums, such as between greater than 45 phr and 120 phr of the resin or alternatively between greater than 45 phr and 90 phr or between 55 phr and 90 phr of the resin.

[0024] In addition to the phenolic terpene resins, particular embodiments of the rubber compositions disclosed herein include a highly unsaturated diene rubber component and in other embodiments the rubber composition may include a highly unsaturated functionalized diene rubber component. Diene elastomers or rubbers that are useful for such rubber compositions 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.

[0025] Those 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. %. Natural rubber is a highly unsaturated diene elastomer.

[0026] 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. %.

[0027] Examples of suitable conjugated dienes include, in particular, 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-di(Ci-Cs alkyl)-1,3-butadienes such as, 2,3-dimethyl-1,3-butadiene, 2,3-diethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-isopropyl-
1,3-butadiene, an aryl-1,3-butadiene, 1,3-pentadiene and 2,4-hexadiene. Examples of vinyl-aromatic compounds include styrene, ortho-, meta- and para-methylstyrene, the commercial mixture "vinyltoluene", para-tert-butylstylene, methoxystyrenes, chloro-styrenes, vinylmesitylene, divinylbenzene and vinylnaphthalene.

[0028] The copolymers may contain between 99 wt. % and 20 wt. % of diene units and between 1 wt. % and 80 wt. % of vinyl-aromatic units. The elastomers may have any microstructure, which is a function of the polymerization conditions used, in particular of the presence or absence of a modifying and/or randomizing agent and 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.

[0029] Examples of suitable diene elastomers include polybutadienes, particularly those having a content of 1,2-units of between 4 mol. % and 80 mol. % or those having a cis-1,4 content of more than 80 mol. %, greater than 90 mol. % or greater than 96 mol. %. Also included are polyisoprenes and butadiene/styrene copolymers, particularly those having a styrene content of between 5 wt. % and 50 wt. % or of between 20 wt. % and 40 wt. % and in the butadiene fraction, a content of vinyl-1,2-bonds of between 4 mol. % and 65 mol. %, a content of trans-1,4 bonds of between 20 mol. % and 80 mol. %. Also included are butadiene/isoprene copolymers, particularly those having an isoprene content of between 5 wt. % and 90 wt. % and a glass transition temperature (Tg, measured in accordance with ASTM D3418) of -40° C to -80° C.

[0030] Further included are isoprene/styrene copolymers, particularly those having a styrene content of between 5 wt. % and 50 wt. % and a Tg of between -25° C and -50° C. In the case of butadiene/styrene/isoprene copolymers, examples of those which are suitable include those having a styrene content of between 5 wt. % and 50 wt. % and more particularly between 10 wt. % and 40 wt. %, an isoprene content of between 15 wt. % and 60 wt. %, and more particularly between 20 wt. % and 50 wt. %, a butadiene content of between 5 wt. % and 50 wt. % and more particularly between 20 wt. % and 40 wt. %, a content of 1,2-units of the butadiene fraction of between 4 wt. % and 85 wt. %, a content of trans-1,4 units of the...
butadiene fraction of between 6 wt. % and 80 wt. %, a content of 1,2-plus 3,4-units of the isoprene fraction of between 5 wt. % and 70 wt. %, and a content of trans-1,4 units of the isoprene fraction of between 10 wt. % and 50 wt. %, and more generally any butadiene/styrene/isoprene copolymer having a Tg of between -20°C and -70°C.

[0031] In summary, suitable diene elastomers for particular embodiments of the present invention include highly unsaturated diene elastomers such as 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). Suitable elastomers may also include any of these elastomers being functionalized elastomers.

[0032] Particular embodiments of the present invention may contain only one diene elastomer and/or a mixture of several diene elastomers. While some embodiments are limited only to the use of one or one or more highly unsaturated diene elastomers, other embodiments may include the use of diene elastomers mixed with any type of synthetic elastomer other than a diene elastomer or even with polymers other than elastomers as, for example, thermoplastic polymers.

[0033] As noted previously, particular embodiments of the rubber compositions disclosed herein include those that may be functionalized; i.e., appended with active moieties. Examples of functionalized elastomers include silanol end-chain functionalized elastomers and aminoalkoxy silane group middle-chain functionalized elastomers.

[0034] In the case of the end-chain functionalized highly unsaturated rubber, the rubber is functionalized with a "silanol" function of formula SiOH. Diene elastomers corresponding to this definition are well known and have, for example, been described in the patent US 6,013,718, which is hereby fully incorporated by reference. Other documents describing silanol functionalized rubber may also be found in WO 2008/141702, WO 2006/050486, EP 0 877 047 B1 or EP 1 400 559 B1.

[0035] The functional group may take the form as a single silanol or a polysiloxane block having a single silanol end. The polysiloxane block may be described as:

\[-(\text{SiR}_2\text{O})_x\text{-H}\]
wherein R\textsubscript{i} and R\textsubscript{2}, that are identical or different, denote an alkyl, cycloalkyl, aryl, alkaryl or vinyl group that has from 1 to 10 carbons and x is an integer of between 1 and 1500 or alternatively, between 1 and 50. In particular embodiments, the silanol function SiOH may take the form of a dimethylsilanol group -SiMe\textsubscript{2}OH. According to particular embodiments of the invention, the silanol function may be bonded to a polysiloxane which constitutes one of the blocks of a block copolymer that also comprises a polydiene block, as described for example in patent US 6,013,718.

[0036] In the case of the middle-chain functionalized highly unsaturated rubber, the functional group is an aminoalkoxyxilane group, that is, the functional group includes an amine functionality in addition to the silanol functionality. Diene elastomers corresponding to this definition are well known and have, for example, been described in the patent application US2011/0178233, which is hereby fully incorporated by reference. In particular embodiments the amine may be primary, secondary or tertiary and in some embodiments the amine is limited to a tertiary amine. The mid-chain functionality attached to the elastomer by the Si may be, for example, HO-Si-Me\textsubscript{3}-N(CH\textsubscript{2}CH\textsubscript{3})\textsubscript{2}, wherein each of the CH\textsubscript{2}CH\textsubscript{3} moieties are bound to the N to provide a tertiary amine. More specifically, in particular embodiments the mid-chain functionality may be expressed as HO-Si-R\textsubscript{i}-NR\textsubscript{2}R\textsubscript{3}, wherein R\textsubscript{2} and R\textsubscript{3} are each bound to the N to provide a tertiary amine. In particular embodiments, R\textsubscript{i} may be a linear or branched C\textsubscript{i}-C\textsubscript{10} alkyl, a C\textsubscript{6}-C\textsubscript{8} aryl derivative, a C\textsubscript{1}-C\textsubscript{5} alkyl or a C\textsubscript{2}-C\textsubscript{4} alkyl. R\textsubscript{2} and R\textsubscript{3} may be the same or different and may be a H atom, a linear or branched C\textsubscript{1}-C\textsubscript{10} alkyl, a C\textsubscript{6}-C\textsubscript{8} aryl derivative, a C\textsubscript{1}-C\textsubscript{5} alkyl or a C\textsubscript{2}-C\textsubscript{4} alkyl. Other examples of documents describing silanol and amine functionality include EP 1 457 501 BI, WO 2006/076629, EP 0 341 496 BI and WO 2004/111094.

[0037] As a functionalizing agent that gives rise to the synthesis of an elastomer bearing an alkoxysilane function and an amine function, examples include N,N-dialkylaminopropyltrialkoxyxilanes, cyclic azadialkoxyxilanes such as N-alkyl-azadialkoxyxilacycloalkanes, 2-pyridylethyltrialkoxyxilanes, 3-carbazolethyltrialkoxy-silanes, 3-alkylideneaminopropyltrialkoxyxilanes, N-trialkoxyxilypropylmorpholines, especially 3-(N,N-dimethylaminopropyl)trimethoxysilane, 3-(1,3-dimethylbutyldiene)-aminopropyltrieth-
oxysilane, N-n-butyl-aza-2,2-dimethoxysilacyclopentane, 2-(4-pyridylethyl)-triethoxysilane and 2-(trimethoxysilyl)pyridine.

[0038] Examples of suitable functionalized highly unsaturated diene elastomers include SBR and/or BR. In particular embodiments of the rubber compositions disclosed herein, the highly unsaturated middle-functionalized elastomer may be an SBR, a BR or combinations thereof. Likewise in particular embodiments the highly unsaturated end-functionalized elastomer may be an SBR, a BR or combinations thereof. It may be useful in some embodiments to limit the highly unsaturated middle-functionalized elastomer and/or the highly unsaturated end-functionalized elastomer to just an SBR or just a BR. In other embodiments, the rubber compositions may include mixtures of a non-functionalized rubber component, a functionalized component or combinations thereof.

[0039] In addition to the rubber components and terpene phenolic resin described above, the rubber composition disclosed herein may further include a reinforcing filler. Reinforcing fillers are added to rubber compositions to, *inter alia*, improve their tensile strength and wear resistance. Any suitable reinforcing filler may be suitable for use in compositions disclosed herein including, for example, carbon blacks and/or inorganic reinforcing fillers such as silica, with which a coupling agent is typically associated. As noted below, there are embodiments of the rubber composition that include very little or no carbon black such as, for example, between 1 phr and 15 phr of carbon black or between 1 phr and 10 phr of carbon black.

[0040] For those embodiments that contain carbon black, suitable carbon blacks include, for example, those of the type HAF, ISAF and SAF, conventionally used in tires. Reinforcing blacks of ASTM grade series 100, 200 and/or 300 are suitable such as, for example, the blacks N115, N134, N234, N330, N339, N347, N375 or alternatively, depending on the intended application, blacks of higher ASTM grade series such as N660, N683 and N772.

[0041] Inorganic reinforcing fillers include any inorganic or mineral fillers, whatever its color or origin (natural or synthetic), that are capable without any other means, other than an intermediate coupling agent, or reinforcing a rubber composition intended for the manufacture of tires. Such inorganic reinforcing fillers can replace conventional tire-grade
carbon blacks, in whole or in part, in a rubber composition intended for the manufacture of
tires. Typically such fillers may be characterized as having the presence of hydroxyl (-OH) groups on its surface.

[0042] Inorganic reinforcing fillers may take many useful forms including, for example, as powder, microbeads, granules, balls and/or any other suitable form as well as mixtures thereof. Examples of suitable inorganic reinforcing fillers include mineral fillers of the siliceous type, such as silica (SiO2), of the aluminous type, such as alumina (Al2O3) or combinations thereof.

[0043] Useful silica reinforcing fillers known in the art include fumed, precipitated and/or highly dispersible silica (known as "HD" silica). Examples of highly dispersible silicas include Ultrasil 7000 and Ultrasil 7005 from Degussa, the silicas Zeosil 1165MP, 1135MP and 1115MP from Rhodia, the silica Hi-Sil EZ150G from PPG and the silicas Zeopol 8715, 8745 and 8755 from Huber. In particular embodiments, the silica may have a BET surface area, for example, of between 60 m²/g and 250 m²/g or alternatively between 80 m²/g and 230 m²/g.

[0044] Examples of useful reinforcing aluminas are the aluminas Baikalox A125 or CR125 from Baikowski, APA-100RDX from Condea, Aluminoxid C from Degussa or AKP-G015 from Sumitomo Chemicals.

[0045] For coupling the inorganic reinforcing filler to the diene elastomer, a coupling agent that is at least bifunctional provides a sufficient chemical and/or physical connection between the inorganic reinforcement filler and the diene elastomer. Examples of such coupling agents include bifunctional organosilanes or polyorganosiloxanes. Such coupling agents and their use are well known in the art. The coupling agent may optionally be grafted beforehand onto the diene elastomer or onto the inorganic reinforcing filler as is known. Otherwise it may be mixed into the rubber composition in its free or non-grafted state. One useful coupling agent is X 50-S, a 50-50 blend by weight of Si69 (the active ingredient) and N330 carbon black, available from Evonik.

[0046] In the rubber compositions according to the invention, the coupling agent may be included at any suitable amount for the given application, examples of which are between 2 phr and 15 phr or alternatively, between 2 phr and 12 phr. It is generally desirable
to minimize its use. In particular embodiments, the amount of coupling agent may represent between 0.5 and 15 wt. % relative to the total weight of the silica filler. In the case for example of tire treads for passenger vehicles, the coupling agent may be less than 12 wt. % or even less than 8 wt. % relative to the total weight of the silica filler.

[0047] In particular embodiments, the amount of total reinforcing filler (carbon black (if used) and/or reinforcing inorganic filler) may include any suitable amount for the given application, examples of which are between 20 phr and 200 phr or alternatively between 50 phr and 150 phr, between 50 phr and 120 phr, between 50 phr and 100 phr or between 60 phr and 110 phr of reinforcing filler.

[0048] As noted above particular embodiments provide that carbon black is explicitly excluded as a filler from the useful rubber compositions disclosed herein. However, in some embodiments a very small quantity may be included to provide coloring (black) to the tire composition and/or UV protection. Such benefits may be obtained by adding at least 0.5 phr but no more than 20 phr of carbon black or alternatively, less than 10 phr, less than 5 phr or between 0.5 phr and 10 phr of carbon black.

[0049] In addition to the diene elastomer, the terpene phenolic resin and the reinforcing filler, particular embodiments of the rubber composition disclosed herein may further include a plasticizing liquid. The plasticizing liquid may provide both an improvement to the processability of the rubber mix and/or a means for adjusting the rubber composition's glass transition temperature and/or its rigidity.

[0050] 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 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.

[0051] 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.

[0052] 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 0 or 10 phr and 60 phr or alternatively, between 0 or 10 phr and 50 phr, between 0 or 5 phr and 40 phr or between 0 or 10 phr and 40 phr. In particular embodiments, there may be no plasticizing liquid utilized.

[0053] 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 0.4 phr and 10 phr or alternatively between 0.4 phr and 5 phr or between 0.5 phr and 2 phr. Particular embodiments may include no free sulfur added in the curing system but instead include sulfur donors.

[0054] 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.
Particular embodiments may include as a secondary accelerator 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).

Without limiting the invention, such accelerators may be added in an amount of up to 5 phr, between 0.5 and 4 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.

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 0.5 phr and 5 phr.

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.

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.
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.

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 is recognized by those skilled in the art, a tread may be manufactured in layers, such as a cap and base design, wherein the cap is the portion that contacts the road and the base is another, typically softer material. The rubber compositions disclosed herein may, in particular embodiments of treads, be limited for use as the layer that contacts the road or other running surface. 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.

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.

Modulus of elongation (MPa) was measured at 10% (MA10) 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.

Mooney viscosity (ML 1+4) was measured in accordance with ASTM Standard D1646-04. In general, the composition in an uncured state is molded in a cylindrical enclosure and heated to 100 °C. After 1 minute of preheating, the rotor turns within the test sample at 2 rpm, and the torque used for maintaining this movement is measured after 4
minutes of rotation. The Mooney viscosity is expressed in "Mooney units" (MU, with 1 MU=0.83 Newton-meter).

[0065] Hysteresis losses (HL) were measured in percent by rebound at 60 °C at the sixth impact in accordance with the following equation:

\[ \text{HL(\%)} = 100(\text{Wo-Wi})/\text{Wi}, \]

where Wo is the energy supplied and Wi is the energy restored.

[0066] Dynamic properties (Tan delta 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* and Tan delta at 60° C were captured.

[0067] Wet braking for a tire mounted on an automobile fitted with an ABS braking system was determined by measuring the distance necessary to go from 50 MPH to 0 MPH upon sudden braking on an asphalt surface having a water depth of about 1.2 mm. A value greater than that of the control, which is arbitrarily set to 100, indicates an improved result, that is to say a shorter braking distance.

[0068] Dry braking for a tire mounted on an automobile fitted with an ABS braking system was measured by determining the distance necessary to go from 60 mph to a complete stop upon sudden braking on a dry asphalt surface. A value greater than that of the control, which is arbitrarily set to 100, indicates an improved result, i.e., a shorter braking distance and improved dry grip.

[0069] Damp braking for a tire mounted on an automobile fitted with an ABS braking system was determined by measuring the distance necessary to go from 40 MPH to 0 MPH upon sudden braking on an asphalt surface wetted to a depth not exceeding the track surface roughness. A value greater than that of the control, which is arbitrarily set to 100, indicates an improved result, that is to say a shorter braking distance.
Example 1

[0070] Rubber compositions were prepared using the components shown in Table 1. The amount of each component making up the rubber compositions shown in Table 1 are provided in parts per hundred parts of rubber by weight (phr).

[0071] The functionalized SBR was an end-chain functionalized SBR with an end-chain functionality of a silanol and a glass transition temperature of -65 °C. The SBR was functionalized with the dimethylsилanol group prepared according to the process described in US 6,013,718.

[0072] The C5-C9 resin was a resin obtained from ExxonMobil as OPERA 373 having a glass transition temperature of -45 °C. The terpene phenolic resins 1, 2, 3 and 4 were obtained from Arizona Chemical and had number average molecular weights of 642 g/mol, 643 g/mol, 600 g/mol and 620 g/mol respectively; had glass transition temperatures of 80 °C, 81 °C, 75 °C and 78 °C respectively; and had hydroxyl numbers of 32 mg KOH/g, 61 mg KOH/g, 134 mg KOH/g and 90 mg KOH/g respectively.

[0073] The plasticizing oil was AGRI-PURE 80. The silane coupling agent was Si69 available from Evonik Degussa. The silica was Zeosil 160ji. The curatives included accelerators, zinc oxide and stearic acid. The additives included wax and 6PPD.

Table 1 – Formulations and Physical Properties

<table>
<thead>
<tr>
<th>Formulations</th>
<th>W1</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
</tr>
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<tbody>
<tr>
<td>f-SBR</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>N234</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
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<tr>
<td>Silica</td>
<td>90</td>
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<td>90</td>
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<tr>
<td>Si69</td>
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<td>7.2</td>
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</tr>
<tr>
<td>Oil</td>
<td>24</td>
<td>24</td>
<td>32</td>
<td>37</td>
</tr>
<tr>
<td>C5-C9 Resin</td>
<td>46</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TP Resin 1</td>
<td></td>
<td>46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TP Resin 2</td>
<td></td>
<td></td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>TP Resin 3</td>
<td></td>
<td></td>
<td></td>
<td>67</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
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<tr>
<td>Curatives and Additives</td>
<td>12.5</td>
<td>12.5</td>
<td>12.5</td>
<td>12.5</td>
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<tr>
<td>Physical Properties</td>
<td></td>
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<tr>
<td>Mooney</td>
<td>70.7</td>
<td>75.8</td>
<td>74.7</td>
<td>71.4</td>
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<td>MA10, MPa</td>
<td>2.9</td>
<td>3.1</td>
<td>3.8</td>
<td>3.9</td>
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<td>Hysteresis Rebound</td>
<td>21.3</td>
<td>21.9</td>
<td>30.3</td>
<td>31.2</td>
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<td>Shear Modulus G* @ 60 °C</td>
<td>0.76</td>
<td>0.79</td>
<td>0.82</td>
<td>0.86</td>
</tr>
<tr>
<td>Tan Delta @ 60 °C</td>
<td>0.139</td>
<td>0.143</td>
<td>0.205</td>
<td>0.220</td>
</tr>
</tbody>
</table>
The rubber formulations were prepared by mixing the components given in Table 1, except for the sulfur and the accelerators, in a Banbury mixer operating between 25 and 65 RPM until a temperature of between 130° C and 170° C was reached. The accelerators and sulfur were added in the second phase on a mill. Vulcanization was effected at 150° C for 40 minutes. The formulations were then tested to measure their physical properties, the results of which are also shown in Table 1.

It is noted that the Mooney viscosity of the formulations using the terpene phenolic resins did not appreciably increase over the witness formulation W1.

Example 2

Using the formulations made in Table 1, tires were built having treads made from these formulations. The tires were an All Season tire of size 205/55R16 91V. The tires were tested for wet braking, damp braking and dry braking as described above. The tire testing results are shown in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>W1</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
</tr>
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<tbody>
<tr>
<td>Wet Braking</td>
<td>100</td>
<td>106</td>
<td>110</td>
<td>109</td>
</tr>
<tr>
<td>Damp Braking</td>
<td>100</td>
<td>103</td>
<td>106</td>
<td>104</td>
</tr>
<tr>
<td>Dry Braking</td>
<td>100</td>
<td>100</td>
<td>108</td>
<td>106</td>
</tr>
</tbody>
</table>

As the tire results demonstrate, the tires provided improved braking over the witness formulation, especially with compositions F2 and F3 that had hydroxyl numbers of 61 mg KOH/g and 134 mg KOH/g respectively having improved performance in each of the braking categories. Using the tan δ at 60 °C lab results as an indicator of improved braking, the trend of improved braking is demonstrated by the tire testing results.

Example 3

Rubber compositions were prepared using the components shown in Table 2. The amount of each component making up the rubber compositions shown in Table 2 are provided in parts per hundred parts of rubber by weight (phr). The materials are the same as those described in Example 1 except as follows. The materials were prepared in the manner provided in Example 1.
[0079] The non-functionalized SBR (Compositions W2 and F4-F6) had a glass transition temperature of -48 °C and the BR had a glass transition temperature of -108 °C.

<table>
<thead>
<tr>
<th>Formulations and Physical Properties</th>
</tr>
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<tbody>
<tr>
<td><strong>Formulations</strong></td>
</tr>
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<td>SBR</td>
</tr>
<tr>
<td>BR</td>
</tr>
<tr>
<td>N234</td>
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<tr>
<td>Silica</td>
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<tr>
<td>Si69</td>
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<tr>
<td>C5-C9 Resin</td>
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<tr>
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</tr>
<tr>
<td>TP Resin 4</td>
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<tr>
<td>TP Resin 3</td>
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<tr>
<td>Sulfur</td>
</tr>
<tr>
<td>Curatives and Additives</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shear Modulus G' @ 60 °C</td>
</tr>
<tr>
<td>Tan Delta @ 60 °C</td>
</tr>
</tbody>
</table>

[0080] Using the tan delta @ 60 °C as an indicator of improved braking, these results demonstrate that improved braking characteristics are expected as the hydroxyl number increases in the terpene phenol resins.

[0001] 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."
[0002] 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 tire tread comprising a rubber composition that is based upon a cross-linkable elastomer composition, the cross-linkable elastomer composition comprising, per 100 parts by weight of rubber (phr):
   
   a highly unsaturated rubber;
   a reinforceing filler; and
   
   a curing system.

2. The tire tread of claim 1, wherein the highly unsaturated rubber is end-chain functionalized with a silanol group.

3. The tire tread of claim 2, wherein the cross-linkable elastomer composition comprises 100 phr of the end-chain functionalized rubber.

4. The tire tread of claim 2 or 3, wherein the end-chain functionalized rubber is a styrene-polybutadiene rubber.

5. The tire tread of any of the preceding claims, wherein the cross-linkable elastomer composition further comprises:

   a second highly unsaturated rubber selected from polybutadiene, natural rubber, styrene-butadiene rubber or combinations thereof.

6. The tire tread of any of the preceding claims, wherein a hydroxyl content of the terpene phenolic resin is between 50 mg KOH/g and 200 mg KOH/g.

7. The tire tread of claim 6, wherein the hydroxyl content of the terpene phenolic resin is between 60 mg KOH/g and 150 mg KOH/g.
8. The tire tread of any of claims 1 through 7 claims, wherein the terpene phenolic resin is between 55 phr and 90 phr.

9. The tire tread of any of the preceding claims, wherein the reinforcing filler is between 50 phr and 150 phr.

10. The tire tread of any of the preceding claims, wherein the reinforcing filler is between 60 phr and 110 phr.

11. The tire tread of any of the preceding claims, wherein the reinforcing filler includes no more than 15 phr of carbon black.

12. The tire tread of any of the preceding claims, wherein the reinforcing filler includes between 1 phr and 10 phr of carbon black.

13. The tire tread of any of the preceding claims, wherein the plasticizing oil is a vegetable oil.

14. The tire tread of claim 13, wherein the vegetable oil has an oleic acid content of at least 70 weight percent.
# INTERNATIONAL SEARCH REPORT

**PCT/US2015/067777**

## A. CLASSIFICATION OF SUBJECT MATTER

**INV. B60C1/00**

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

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

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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* 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
- "Z" document member of the same patent family

Date of the actual completion of the international search

21 March 2016

Date of mailing of the international search report

31/03/2016

Name and mailing address of the ISA/

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NL - 2280 HV Rijswijk
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Authorized officer

Trauner, H

X See patent family annex.

Further documents are listed in the continuation of Box C.
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