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(54) Title: LOW HYSTERESIS TIRE

(57) Abstract: Embodiments of the present invention include tires and other rubber articles comprising a material that is based upon a cross-linkable rubber composition, the cross-linkable rubber composition comprising, per 100 parts by weight of rubber, a tin-functionalized highly unsaturated diene rubber, between 5 phr and 30 phr of a vegetable oil, carbon black and a sulfur vulcanization system



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LOW HYSTERESIS TIRE

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] This invention relates generally to rubber articles and more particularly, to tires and the rubber compositions that are used to manufacture tires.

Description of the Related Art

[0002] A vehicle tire is made up of a number of parts or components, each of which has a specific function to perform in the tire. Typically a tire includes a pair of beads in the form of hoops for anchoring the ply and for providing a means for locking the tire onto the wheel assembly. The ply, extending from bead to bead, is comprised of cords that serve as the primary reinforcing material in the tire casing. The tire further includes belts extending circumferentially around the tire under the tread for stiffening the casing and the tread. The tread is that portion of the tire that contacts the road or other driving surface. The sidewall of the tire protects the ply or plies from road hazards and ozone and is typically the outermost rubber component of the tire extending between the tread and the bead.

[0003] Some tire treads are of a cap/undertread construction, with the cap designed to be ground-contacting with an outer surface configured with lugs and grooves and with the undertread designed to be underlying and supporting the cap. The undertread is therefore positioned between the tread cap and the tire carcass. The undertread is not intended to be ground-contacting and therefore is not intended to have the same properties as the cap, *e.g.*, good traction and good treadwear.

[0004] Each of these components of a tire is typically made up of rubber compositions that include one or more of the following materials: rubber elastomers, fillers such as carbon black and/or silica, plasticizers, vulcanization packages and antidegradants. The tire industry constantly endeavors to reduce the hysteresis of such rubber compositions in order to lower fuel consumption and thus conserve the environment. Lowering the hysteresis of a rubber composition used to manufacture a tire tends to reduce the rolling resistance of a tire.

[0005] There is a need for developing materials having lowered hysteresis that are suitable for manufacturing tire components without compromising other desired properties of the tire.

SUMMARY OF THE INVENTION

[0006] Embodiments of the present invention include tires and other rubber articles comprising a material that is based upon a cross-linkable rubber composition, the cross-linkable rubber composition comprising, per 100 parts by weight of rubber, a tin-functionalized highly unsaturated diene rubber, between 5 phr and 30 phr of a vegetable oil, carbon black and a sulfur vulcanization system.

[0007] 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

[0008] Embodiments of the present invention include rubber compositions and articles made from these rubber compositions, such articles including tires and tire components such as treads, sidewalls and skims. These rubber compositions comprise a tin functionalized highly unsaturated rubber elastomer with a vegetable oil added as a plasticizer. Surprisingly, when the vegetable oil is added to a rubber composition having a tin functionalized highly unsaturated rubber elastomer, the hysteresis of the rubber composition is significantly reduced compared to similar rubber compositions containing a traditional aromatic oil as a plasticizer.

[0009] It should be noted that the rubber articles, including tire components, discussed herein are made from a material that is based upon a cross-linkable rubber composition containing a vegetable oil and a tin functionalized highly unsaturated rubber elastomer. The term "based upon" as used herein recognizes that the tire components or other rubber articles 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 the cross-linkable rubber composition.

[0010] Considering first the vegetable oils that may be added to the rubber compositions disclosed herein, such vegetable oils are made up in large part of fatty acids having 16 or 18 carbon atoms. These fatty acids may be saturated fatty acids, *i.e.*, they contain no carbon-carbon double bonds, or they may be unsaturated fatty acids having, for example, one, two or three sets of carbon-carbon double bonds. One example of a saturated fatty acid having 16 carbon atoms found in some vegetable oils is palmitic acid and one with 18 carbon atoms is stearic acid. Oleic acid is an 18-carbon monounsaturated fatty acid (having one double bond) while linoleic and linolenic acids are 18-carbon polyunsaturated fatty acids (having two and three double bonds respectively) that can be found in some vegetable oils.

[0011] Suitable vegetable oils that can be used in the particular embodiments of the present invention include, for example, sunflower oil, soybean oil, safflower oil, corn oil, linseed oil and cotton seed oil. These oils and other such oils may be used singularly or in combination. In some embodiments, sunflower oil having a high oleic acid content is used alone. An example of a sunflower oil having high oleic acid content is AGRI-PURE 80, available from Cargill with offices in Minneapolis, MN.

[0012] In particular embodiments a vegetable oil is selected having an oleic acid content of at least 60 weight percent oleic acid or alternatively, at least 70 weight percent oleic acid or at least 80 weight percent oleic acid. The vegetable oil may be added to the rubber composition in an amount of between 1 and 30 parts per hundred parts of rubber by weight (phr) or alternatively between 5 phr and 30 phr, between 5 phr and 20 phr or between 3 phr and 15 phr.

[0013] The rubber compositions disclosed herein that are useful for the manufacture of articles and tire components, such as the sidewalls, treads, tread caps, undertreads and rubber-based skims that cover the cords and belts of tires, include a highly unsaturated diene elastomer and vegetable oil. Particular embodiments of the invention include a tin-functionalized highly unsaturated diene elastomer. In some embodiments, the tin functionalized elastomer is a styrene-butadiene tin functionalized elastomer.

[0014] Tin-functionalized elastomers, when included in rubber compositions used to manufacture tires, are known to provide desirable properties to tires such as improved tread wear and reduced rolling resistance. Such tin-functionalized elastomers can be made by coupling the rubber polymer with a tin coupling agent at or near the end of the polymerization used in synthesizing the rubber elastomer. In the coupling process, live polymer chain ends react with the tin coupling agent thereby coupling the elastomer.

[0015] The tin-functionalized highly unsaturated elastomers useful in the present invention may be used in particular embodiments alone or in combination with other diene elastomers. In general, diene elastomers or rubber is understood to mean those elastomers resulting at least in part (*i.e.*, a homopolymer or a copolymer) from diene monomers (monomers bearing two double carbon-carbon bonds, whether conjugated or not). Essentially unsaturated diene elastomers are understood to mean those diene elastomers that result at least in part from conjugated diene monomers, having a content of members or units of diene origin (conjugated dienes) that are greater than 15 mol.%.

[0016] Thus, for example, diene elastomers such as butyl rubbers, nitrile rubbers or copolymers of dienes and of alpha-olefins of the ethylene-propylene diene terpolymer (EPDM) type or the ethylene-vinyl acetate copolymer type do not fall within the preceding definition, and may in particular be described as "essentially saturated" diene elastomers (low or very low content of units of diene origin, *i.e.*, less than 15 mol. %). Particular embodiments of the present invention include no essentially saturated diene elastomers.

[0017] Within the category of essentially unsaturated diene elastomers are the highly unsaturated diene elastomers, which are understood to mean in particular diene elastomers having a content of units of diene origin (conjugated dienes) that is greater than 50 mol.%. Particular embodiments of the present invention may include not only no essentially saturated diene elastomers but also no essentially unsaturated diene elastomers that are not highly unsaturated.

[0018] The rubber elastomers suitable for use with particular embodiments of the present invention include highly unsaturated diene elastomers, for example, polybutadienes (BR), polyisoprenes (IR), natural rubber (NR), butadiene copolymers, isoprene copolymers and mixtures of these elastomers.

[0019] Also suitable for use in particular embodiments of the present invention are rubber elastomers that are copolymers and include, for example, butadiene-styrene copolymers (SBR), butadiene-isoprene copolymers (BIR), isoprene-styrene copolymers (SIR) and isoprene-butadiene-styrene copolymers (SBIR), mixtures thereof and/or with other essentially unsaturated and/or highly unsaturated rubber elastomers.

[0020] Also suitable for use in particular embodiments of the present invention are rubber elastomers that include, for example, natural rubber, synthetic cis-1,4 polyisoprenes and mixtures thereof and/or with other essentially unsaturated and/or highly unsaturated rubber elastomers. These synthetic cis-1,4 polyisoprenes may be characterized as possessing cis-1,4 bonds at more than 90 mol.% or alternatively, at more than 98 mol.%.

[0021] Between 50 phr and 100 phr of the tin-functionalized elastomer may be included in the rubber compositions disclosed herein. Alternatively, the tin-functionalized elastomer may be added in an amount of between 60 phr and 100 phr, between 70 phr and 90 phr, between 80 phr and 90 phr, between 90 phr and 100 phr, between 80 phr and 100 phr or 100 phr. In particular embodiments, these amounts of tin-functionalized elastomers may include solely styrene-butadiene tin-functionalized elastomer or alternatively may include solely other tin-functionalized highly unsaturated diene elastomers or combinations of tin-functionalized highly unsaturated diene elastomers. In one embodiment, for example, the rubber composition includes 85 phr of tin-functionalized styrene-butadiene rubber and 15 phr of natural rubber.

[0022] In addition to the tin-functionalized highly unsaturated rubber and vegetable oil, particular embodiments of the present invention include carbon black. Any carbon black is useful for the rubber compositions of the present invention as long as it is suitable for the particular application. Suitable carbon blacks that may be used in particular embodiments of the present invention include the blacks of the type HAF, ISAF and SAF, which are conventionally used in tires, and particularly in treads for these tires. Non-limitative examples of such blacks may include N115, N134, N234, N339, N347, N375, and the 600 series, including, but not limited to, N630, N650 and N660. The amount of carbon black present in the total reinforcing filler may vary within wide limits, *e.g.*, between 5 and 100 phr or between 20 and 80 phr or between 30 and 70 phr. Alternatively, in some embodiments, as

well known in the art, the carbon black may be added to the rubber composition with the addition of an inorganic reinforcing filler, such as silica, although some embodiments of the present invention include no additional filler other than carbon black.

[0023] The rubber compositions disclosed herein 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 0.1 phr and 4 phr. Some embodiments include no free sulfur added in the curing system but instead include sulfur donors.

[0024] 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). Particular embodiments utilize CBS solely as the sulfenamide accelerator. 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.

[0025] 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.

[0026] 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 2 phr and 4 phr. Waxes may be added in an amount, for example, of between 1 phr and 5 phr.

[0027] Particular embodiments of the present invention include tires and tire components intended for passenger-car or light truck tires, trucks and heavy vehicles. Indeed the rubber compositions disclosed herein are intended for particular embodiments that may include tire components that may be fitted on motor vehicles or non-motor vehicles such as bicycles, motorcycles, racing cars, industrial vehicles such as vans, heavy vehicles such as buses and trucks, off-road vehicles such as agricultural, mining, and construction machinery, aircraft or other transport or handling vehicles.

[0028] The rubber compositions disclosed herein may be used in particular embodiments for various rubber products such as a tread compound, undertread compound, sidewall compound, wire skim compound, inner liner compound, bead, apex, any compound used in a tire carcass, including carcass reinforcement and in other components for tires, industrial rubber products, seals, timing belts, power transmission belting, and other rubber goods. As such, the particular embodiments of the present invention include products made from the rubber composition disclosed herein.

[0029] 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.

[0030] **Moduli of elongation** (MPa) were measured at 10% (MA10), 100% (MA 100) and at 300% (MA 300) at a temperature of 23 °C based on ASTM Standard D412 on dumb bell test pieces. The measurement 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.

[0031] **Tear Resistance (TR):** The tear resistance indices are measured at 100 °C. The breaking load in N/mm of thickness and the elongation at break in percentage are measured on a test piece of dimensions 10 x 142 x 2.5 mm notched (perpendicular to the tear

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direction) with 3 notches that each have a depth of 3 mm. The tear resistance index is then provided by the following equation: $TR = (FRD * ARD) / 100$. The higher the index for a material, the less susceptible is the material to tearing.

[0032] **Dynamic characteristics** of the materials were measured on an MTS 831 Elastomer Test System in accordance with ASTM D5992. The response of a sample of vulcanized material (cylindrical test piece of a thickness of 4 mm and a section of 400 mm²), subjected to an alternation single sinusoidal shearing stress, at a frequency of 10 Hz and at 80 °C, is recorded. Scanning is effected at an amplitude of deformation of 0.1 to 50% (outward cycle), then of 50% to 0.1% (return cycle). The shear modulus G^* at 20% deformation in MPa and the maximum value of the tangent of the loss angle $\tan \delta$ (max $\tan \delta$) was determined during the return cycle.

Example 1

[0033] This example provides comparisons between rubber compositions with the tin-functionalized SBR having vegetable oil used as a plasticizer with those having high aromatic oil used as a plasticizer. As the results show, the hysteresis of the material having the vegetable oil is surprisingly significantly less than the hysteresis of the material having the high aromatic oil as a plasticizer.

[0034] Two thermochemical stages were used to prepare the rubber compositions having the material components shown in Table 1 (amounts shown in phr). First, the elastomers, the carbon black and the plasticizing oil were introduced into a 3.4 liter Banbury-type mixer in the amounts shown in Table 1. The material was mixed until a temperature of between 145 °C and 170 °C was reached. The mixture was then dropped and cooled to a temperature below 100 °C.

Table 1 – Rubber Formulations (phr) and Physical Properties

Formulations	W1	F1	F2	W2	F3	F4
Natural Rubber	15	15	15	15	15	15
Tin Functionalized SBR	85	85	85			
Non-functionalized SBR				85	85	85
AGRI-PURE 80 Sunflower Oil		10.7	8.7		10.7	8.7
Hi Aromatic Oil	11.7			11.7		
Carbon Black N234	67	67	67	67	67	67
Paraffin	1	1	1	1	1	1

Curing Package	4.1	4.1	4.1	4.1	4.1	4.1
Sulfur	0.85	0.85	0.85	0.85	0.85	0.85
Physical Properties						
MA10, (MPa)	5.8	4.9	5.7	6.2	5.7	5.6
MA100, (MPa)	2.2	1.9	2.3	2.2	2.1	2.2
MA300, (MPa)	2.9	2.5	2.9	2.6	2.5	2.7
Tear Resistance Index	44	49	49	105	99	109
G* 20% p-p, 10 Hz, (MPa)	1.8	1.6	1.7	1.8	1.7	1.7
Max tan δ (80 °C)	0.21	0.17	0.18	0.26	0.24	0.24

[0035] In the second thermochemical stage, the cooled mixture was transferred to a mill having two cylinders that operated at a speed of 30 RPM. The vulcanizing agents were added and mixing continued until the vulcanizing agents were well dispersed. The rubber compositions were rolled into sheets and cured for the 30 minutes at a temperature of 150 °C for all the materials. The cured sheets were then cut into testing pieces suitable for the testing methods utilized to determine the physical characteristics of the examples.

[0036] The two witness formulations (W1, W2) shown in Table I include the high aromatic oil as the plasticizer. The aromatic oil was VALARO 130A from Valero Co. and had an aromatic content of about 40% per ASTM test method D2140. The first witness formulation, W1, includes a tin-functionalized SBR elastomer while the second witness formulation, W2, includes a non-functionalized SBR elastomer. For comparison, two of the formulations (F1, F2) include the tin-functionalized SBR elastomer with the vegetable oil while the other two formulations (F3, F4) include the non-functionalized SBR elastomer with the vegetable oil.

[0037] 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.”

[0038] 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 comprising a material that is based upon a cross-linkable rubber composition, the cross-linkable rubber composition comprising, per 100 parts by weight of rubber:
 - a tin-functionalized highly unsaturated diene rubber;
 - between 5 phr and 30 phr of a vegetable oil;
 - carbon black; and
 - a sulfur vulcanization system.
2. The tire of claim 1, wherein the vegetable oil is sunflower oil.
3. The tire of claim 1, wherein the vegetable oil is selected from sunflower oil, soybean oil, safflower oil, corn oil, linseed oil, cotton seed oil or combinations thereof.
4. The tire of claim 1, wherein the cross-linkable rubber composition comprises between 20 phr and 100 phr of the tin-functionalized highly unsaturated diene rubber.
5. The tire of claim 1, wherein the cross-linkable rubber composition comprises between 30 phr and 100 phr of the tin-functionalized highly unsaturated diene rubber.
6. The tire of claim 1, wherein the cross-linkable rubber composition comprises between 50 phr and 100 phr of the tin-functionalized highly unsaturated diene rubber.
7. The tire of claim 1, wherein the cross-linkable rubber composition comprises between 90 phr and 100 phr of the tin-functionalized highly unsaturated diene rubber.
8. The tire of claim 1, wherein the cross-linkable rubber composition comprises 100 phr of a tin-coupled styrene-butadiene rubber.

9. The tire of claim 1, wherein the tin-functionalized highly unsaturated diene rubber is a tin-functionalized styrene-butadiene.
10. The tire of claim 1, further comprising a tread component, the tread manufactured from the cross-linkable rubber composition of claim 1.
11. The tire of claim 1, further comprising a sidewall component, the sidewall component manufactured from the cross-linkable rubber composition of claim 1.
12. The tire of claim 1, wherein the cross-linkable rubber composition further comprising between 1 phr and 80 phr of a highly unsaturated diene elastomer.
13. The tire of claim 13, wherein the highly unsaturated diene elastomer is selected from natural rubber, butadiene rubber, styrene-butadiene rubber, synthetic polyisoprene rubber or combinations thereof.
14. The tire of claim 1, wherein the cross-linkable rubber composition further comprising between 1 phr and 50 phr of a highly unsaturated diene elastomer.
15. The tire of claim 1, wherein the vegetable oil is present in an amount of between 5 phr and 20 phr.
16. The tire of claim 1, wherein the vegetable oil comprises at least 60 percent by weight of oleic acid.
17. The tire of claim 1, wherein the vegetable oil comprises at least 80 percent by weight of oleic acid.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 11/30244

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C08L 91/00 (2011.01)

USPC - 524/313

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)

IPC: C08L 91/00 (2011.01)

USPC: 524/313

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

IPC: C08L 91/00 (2011.01) (text search only)

USPC: 524/313 (text search only)

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

(USPT, PGPB, EPAB, JPAB); Google Patent, Google Scholar

Search terms on extra sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2008/0306199 A1 (Minagawa) 11 Dec 2008 (11.12.2008) (Abstract, para [0023], [0024], [0026], [0028]-[0030], [0035]-[0038], [0043], [0044], [0052], [0053], [0061], [0062], [0066], [0067], [0068], Fig. 1).	1-17
Y	US 2009/0229720 A1 (Serra et al.) 17 Sep 2009 (17.09.2009) (Abstract, para [0024], [0028], [0032], [0034], [0038], [0047], [0049], [0050], [0066]).	1-17

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

* 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

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

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"&" document member of the same patent family

Date of the actual completion of the international search

12 May 2011 (12.05.2011)

Date of mailing of the international search report

24 MAY 2011

Name and mailing address of the ISA/US

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 11/30244

continued from box B

Search terms:

tire, tyre, rubber, tin, tin-functionalized, tin coupling, crosslink, diene, unsaturated, polybutadiene, butadiene, NR, natural rubber, SBR, styrene-butadiene, isoprene, polyisoprene, vegetable oil, sunflower, sun flower, soybean, soya, soy, safflower, corn oil, linseed oil, cottonseed or cotton seed, carbon black, sulfur, sulphur, vulcanization, oleic acid, phr, parts per hundred, tread, sidewall