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(54) Title: ENVIRONMENT-FRIENDLY RUBBER COMPOSITION

(57) Abstract: The present disclosure relates to a cross-linkable rubber composition comprising maleated castor oil as plasticizer. The bio-based maleated castor oil can be used as partial or total replacement of petroleum-based plasticizers used in tire applications.



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ENVIRONMENT-FRIENDLY RUBBER COMPOSITION

FIELD OF THE INVENTION

[0001] The present disclosure relates to environment-friendly rubber compositions intended in particular for the manufacture of tires or tire components, such as tire treads.

BACKGROUND OF THE INVENTION

[0002] The background description includes information that may be useful in understanding the present invention. It is not an admission that any of the information provided herein is prior art or relevant to the presently claimed invention, or that any publication specifically or implicitly referenced is prior art.

[0003] Aromatic hydrocarbon oils obtained from petroleum refining have been known for a long time and are used as plasticizers or extender oils in natural and synthetic rubbers or rubber products. These petroleum-based hydrocarbon oils are used in the tire industry as processing aids to ease compounding of rubber and as plasticizers to modify the mechanical properties of rubber compound after vulcanization. They are also used to reduce Mooney viscosity of synthetic rubbers to ease their compounding with other ingredients of rubber formulations. Enormous amount of plasticizers is sometimes added to rubber mixtures, in order to reduce the cost of the mixture, to improve filler dispersion, and to improve the physical properties of the mixture and of the vulcanizates produced therefrom. Majority of the plasticizers used in the rubber industry are generally based on petroleum. Most commonly used are distillate aromatic extract (DAE) oils, treated distillate aromatic extract (TDAE) oils, mild extract solvate (MES) oils and residual aromatic extract (RAE) oils. The use of petroleum-based hydrocarbon oils as rubber plasticizer, however, is undesirable for environmental reasons due to the possible danger to the environment and inhabitants. Additionally, the use of petroleum-based hydrocarbon oils in the manufacture of tires or rubber products is expected to decline in the coming years because of the continuous rise in the price of crude oil and the high rate of depletion of known petroleum oil reserves. Alternatives used as plasticizers in rubber formulations are vegetable oils. However, when utilizing vegetable oils as rubber plasticizer, their polarity becomes a problem due to the lack of compatibility between the non-polar rubbers and the polar vegetable oils.

[0004] In view of the environmental concerns in relation to the use of petroleum-based plasticizers, there is a high desire to make a new, more environmentally acceptable plasticizer

from renewable sources as partial or total replacement of petroleum-based plasticizers. The present disclosure satisfies these needs and provides further related advantages.

SUMMARY OF THE INVENTION

[0005] Aspects of the present disclosure relate to the use of maleated castor oil as plasticizer for rubber compositions usable for the manufacture of tires or tire components such as tire treads. The bio-based maleated castor oil does not have the disadvantages of petroleum-based plasticizers and may be used to replace a part of the petroleum-based plasticizer or to replace it completely in cross-linkable or cross-linked rubber compositions specifically designed for tire applications. Further, the maleated castor oil has excellent compatibility with natural and synthetic rubbers of non-polar type, thereby allowing to plasticize a wide variety of non-polar rubbers usable in tire applications and to maximize the desired properties of final finished products.

[0006] Accordingly, one aspect of the present disclosure is directed to a cross-linkable rubber composition comprising an elastomer, a filler, and a maleated castor oil. Maleated castor oil is the product of chemical reaction of castor oil and maleic anhydride. In various embodiments, the maleated castor oil can be used in the cross-linkable rubber composition in an amount of from 1 to 20 phr. Preferably, the amount of maleated castor oil is between 7 and 20 phr. The elastomer can be a natural rubber or a synthetic rubber usable for the manufacture of tires or tire components. In some embodiments, the elastomer can be a blend of two or more synthetic rubbers. In one exemplary embodiment, the elastomer is a blend of polybutadiene rubber (PBD) with solution-polymerized styrene-butadiene (SSBR).

[0007] As indicated above, the cross-linkable rubber composition comprises a filler. The filler can be selected from the group consisting of carbon black, silica, aluminosilicates, chalk, titanium dioxide, magnesium oxide, zinc oxide, clay, calcium carbonate, and a mixture thereof. Preferably, filler(s) are present in the cross-linkable rubber composition in an amount of from 30 to 90 phr. In one embodiment, the filler has a BET surface of between 150 and 250 m²/g.

[0008] In various embodiments, the cross-linkable rubber composition can further include a vulcanization system to cause dynamic vulcanization (cross-linking) of the unvulcanised elastomers. The vulcanization system can include at least one cross-linking agent, at least one vulcanization accelerator, at least one vulcanization activator, or a mixture thereof. In one embodiment, the vulcanization system is present in the cross-linkable rubber composition in an amount of from 0.5 to 20 phr.

[0009] In one particularly preferred embodiment, the cross-linkable rubber composition comprises 100 phr of at least one elastomer, 30 to 90 phr of a filler, 1 to 20 phr of maleated castor oil, 0.5 to 5 phr of at least one cross-linking agent, 1 to 7 phr of at least one vulcanization accelerator, and 1 to 8 phr of at least one vulcanization activator.

5 [0010] Another aspect of the present disclosure relates to a cross-linked rubber composition, obtained by cross-linking the cross-linkable rubber composition disclosed herein. The cross-linked rubber composition can be obtained by blending the cross-linkable rubber composition with a vulcanization system to produce a blend, and heating the blend at a predetermined temperature to form the cross-linked rubber composition. In one embodiment,
10 the blend is heated to a temperature from 110° C to 200° C.

[0011] Another aspect of the present disclosure relates to a tire or tire tread, comprising the cross-linked rubber composition disclosed herein.

[0012] Another aspect of the present disclosure relates to a finished or semifinished rubber article, comprising the cross-linked rubber composition disclosed herein.

15 [0013] Various objects, features, aspects and advantages of the inventive subject matter will become more apparent from the following detailed description of preferred embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The accompanying drawings are included to provide a further understanding of
20 the present disclosure, and are incorporated in and constitute a part of this specification. The drawings illustrate exemplary embodiments of the present disclosure and, together with the description, serve to explain the principles of the present disclosure.

[0015] FIG. 1 illustrates a reaction scheme for the preparation of maleated castor oil.

[0016] FIG. 2 shows a comparison of the FTIR spectrum of (unmodified) castor oil to the
25 FTIR spectrum of maleated castor oil produced according to an embodiment of the present disclosure.

DETAILED DESCRIPTION OF THE INVENTION

[0017] The following is a detailed description of embodiments of the present disclosure. The embodiments are in such detail as to clearly communicate the disclosure. However, the
30 amount of detail offered is not intended to limit the anticipated variations of embodiments; on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the present disclosure as defined by the appended claims.

[0018] Unless the context requires otherwise, throughout the specification which follow, the word “comprise” and variations thereof, such as, “comprises” and “comprising” are to be construed in an open, inclusive sense that is as “including, but not limited to.”

[0019] Reference throughout this specification to “one embodiment” or “an embodiment”
5 means that a particular feature, structure or characteristic described in connection with the embodiment is included in at least one embodiment. Thus, the appearances of the phrases “in one embodiment” or “in an embodiment” in various places throughout this specification are not necessarily all referring to the same embodiment. Furthermore, the particular features, structures, or characteristics may be combined in any suitable manner in one or more
10 embodiments.

[0020] As used in the description herein and throughout the claims that follow, the meaning of “a,” “an,” and “the” includes plural reference unless the context clearly dictates otherwise. Also, as used in the description herein, the meaning of “in” includes “in” and “on” unless the context clearly dictates otherwise.

[0021] In some embodiments, the numbers expressing quantities of ingredients, properties such as concentration, process conditions, and so forth, used to describe and claim certain embodiments of the invention are to be understood as being modified in some instances by the term “about.” Accordingly, in some embodiments, the numerical parameters set forth in the written description are approximations that can vary depending upon the
20 desired properties sought to be obtained by a particular embodiment. In some embodiments, the numerical parameters should be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of some embodiments of the invention are approximations, the numerical values set forth in the specific examples are reported as
25 precisely as practicable.

[0022] The recitation of ranges of values herein is merely intended to serve as a shorthand method of referring individually to each separate value falling within the range. Unless otherwise indicated herein, each individual value is incorporated into the specification as if it were individually recited herein.

[0023] All methods described herein can be performed in suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g. “such as”) provided with respect to certain embodiments herein is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention otherwise claimed. No language in the specification

should be construed as indicating any non-claimed element essential to the practice of the invention.

[0024] The headings and abstract of the invention provided herein are for convenience only and do not interpret the scope or meaning of the embodiments.

5 **[0025]** Various terms are used herein. To the extent a term used in a claim is not defined below, it should be given the broadest definition persons in the pertinent art have given that term as reflected in printed publications and issued patents at the time of filing.

[0026] As used herein, the term "phr" refers to parts by weight of the referenced component per 100 parts by weight of total rubber or elastomer in the composition. Such term
10 is commonly used in the rubber compounding art.

[0027] The present disclosure is directed to the use of maleated castor oil as plasticizer for rubber compositions usable for the manufacture of tires or tire components such as tire treads. The bio-based maleated castor oil does not have the disadvantages of petroleum-based plasticizers and may be used to replace a part of the petroleum-based plasticizer or to replace
15 it completely in cross-linkable or cross-linked rubber compositions specifically designed for tire applications. Further, the maleated castor oil has excellent compatibility with natural and synthetic rubbers of non-polar type, thereby allowing to plasticize a wide variety of non-polar rubbers usable in tire applications and to maximize the desired properties of final finished products.

20 **[0028]** Accordingly, one aspect of the present disclosure is directed to a cross-linkable rubber composition comprising an elastomer, a filler, and a maleated castor oil. The cross-linkable rubber composition is useful for the manufacture of tires or tire components such as tire treads, and includes at least one elastomer. Thus, it is considered that the elastomer is a cross-linkable (curable), e.g., vulcanizable, elastomer. The term "elastomer" is often used
25 interchangeably with the term "rubber" or more professional "un-vulcanized rubber". The elastomer can be a natural rubber, a synthetic rubber, a blend of synthetic and natural rubber, or a blend of various synthetic rubbers.

[0029] In one embodiment, the elastomer can be selected from the group consisting of natural rubber (NR), synthetic polyisoprene rubber (IR), polybutadiene rubber (PBD),
30 polyvinyl-butadiene rubber, styrene-butadiene rubber (SBR), solution-polymerized styrene-butadiene rubber (SSBR), emulsion-polymerized styrene-butadiene rubber (ESBR), nitrile rubber (NBR), hydrogenated nitrile rubber, butyl rubber, halogenated butyl rubbers, liquid rubbers, polynorbornene copolymer, isoprene-isobutylene copolymer, chloroprene rubber, ethylene propylene diene monomer rubber (EPDM), acrylate rubber, fluorine rubber, silicone

rubber, polysulfide rubber, epichlorohydrin rubber, a terpolymer formed from ethylene monomers, propylene monomers, and/or ethylene propylene diene monomer (EPDM), styrene-isoprene-butadiene terpolymer, hydrated acrylonitrile butadiene rubber, isoprene-butadiene copolymer, hydrogenated styrene-butadiene rubber, butadiene acrylonitrile rubber, 5 styrene-butadiene-styrene block copolymer (SBS), styrene-ethylene/butylene-styrene block copolymer (SEBS), styrene-[ethylene-(ethylene/propylene)]-styrene block copolymer (SEEPS), styrene-isoprene-styrene block copolymer (SIS), isoprene-based block copolymers, butadiene-based block copolymers, styrenic block copolymers, hydrogenated styrenic block copolymers, styrene butadiene copolymers, polyisobutylene, ethylene vinyl acetate (EVA) 10 polymers, polyolefins, metallocene-catalyzed polyolefin polymers and elastomers, reactor-made thermoplastic polyolefin elastomers, olefin block copolymer, polyurethane block copolymer, polyamide block copolymer, thermoplastic polyolefins, thermoplastic vulcanizates, ethylene vinyl acetate copolymer, ethylene n-butyl acrylate copolymer, ethylene methyl acrylate copolymer, neoprene, urethane, ethylene acrylic acid copolymer, ethylene- 15 propylene polymers, propylene-hexene polymers, ethylene-butene polymers, ethylene octene polymers, propylene-butene polymers, ethylene-propylene-butylene terpolymers, and a mixture thereof.

[0030] In some embodiments, the elastomer is a blend of polybutadiene rubber with a styrene-butadiene rubber. In one exemplary embodiment, the elastomer is a blend of 20 polybutadiene rubber (PBD) with solution-polymerized styrene-butadiene (SSBR). In an embodiment, the cross-linkable rubber composition comprises from 10 to 40 phr of polybutadiene rubber as a blend with from 60 to 90 phr of a styrene-butadiene rubber. In one particularly preferred embodiment, the cross-linkable rubber composition comprises 20 phr of polybutadiene rubber as a blend with 80 phr of a styrene-butadiene rubber.

[0031] As indicated above, the cross-linkable rubber composition comprises maleated 25 castor oil as plasticizer. The maleated castor oil can be used to replace a part of the traditional petroleum-based plasticizer or to replace it completely in cross-linkable or cross-linked rubber compositions specifically designed for tire applications. Maleated castor oil is the product of chemical reaction of castor oil and maleic anhydride. In an embodiment, maleated 30 castor oil (MACO) can be prepared by an esterification reaction between castor oil (CO) and maleic anhydride (MAH) in presence of benzoyl peroxide as a catalyst. It is preferred that the molar ratio of castor oil to maleic anhydride ranges between about 1:1 and 1:3. FIG. 1 depicts a reaction scheme for the preparation of maleated castor oil by reaction of castor oil with maleic anhydride. FIG. 2 shows a comparison of the FTIR spectrum of (unmodified) castor

oil to the FTIR spectrum of maleated castor oil produced according to an embodiment of the present disclosure. The maleated castor oil according to the present disclosure has characteristic FTIR peaks at 3440 cm^{-1} and 1650 cm^{-1} , as determined using ASTM E1252. The maleated castor oil associates with the filler surface and keeps the filler particles adequately and homogeneously dispersed in rubber matrix until curing (cross-linking) takes place, thereby preventing flocculation of filler particles after rubber compounding. As the cross-linkable rubber composition is cured, the reactive C-C double bond of the maleated castor oil chemically bonds to the rubber molecules, which prevents the maleated castor oil from leaching out of the cured (vulcanized) rubber over time. In various embodiments, the maleated castor oil can be used in the cross-linkable rubber composition in an amount of from 1 to 20 phr. Preferably, the amount of maleated castor oil is between 7 and 20 phr.

[0032] As indicated above, the cross-linkable rubber composition includes a reinforcing filler to improve technical requirements of tires, such as high wear resistance, low rolling resistance, or wet grip. While any filler can be used as long as it is compatible with the elastomer, typical fillers include carbon black, silica, aluminosilicates, chalk, titanium dioxide, magnesium oxide, zinc oxide, clay, calcium carbonate, and a mixture thereof. Preferably, silica or carbon black is used as the filler. In one embodiment, the filler is a blend of silica and carbon black. Filler(s) are present in the cross-linkable rubber composition in an amount of from 30 to 90 phr, preferably from 50 to 90 phr. In one embodiment, the filler has a BET surface of between 150 and $250\text{ m}^2/\text{g}$, as measured according to ASTM D6738.

[0033] In various embodiments, the cross-linkable rubber composition can further include a vulcanization system to cause dynamic vulcanization (cross-linking) of the unvulcanized elastomers. The vulcanization system can include at least one cross-linking agent, at least one vulcanization accelerator, at least one vulcanization activator, or a mixture thereof. In one embodiment, the vulcanization system is present in the cross-linkable rubber composition in an amount of from 0.5 to 20 phr.

[0034] While any cross-linking agent known in the art may be used, in preferred embodiments of the present disclosure, sulphur is used. The amount of cross-linking agent is preferably between 0.5 and 5 phr.

[0035] While any vulcanization accelerators can be used, typical accelerators include but not limited to n-cyclohexyl-2-benzothiazole sulfenamide (CBS), diphenyl guanidine (DPG), and combination thereof. Preferably, a mixture of CBS and DPG is used as the vulcanization accelerator. The vulcanization accelerator can be used in an amount ranging from 1 to 7 phr.

[0036] The vulcanization activator can be any activator as would be known to one of skill in the art. Preferably, the activator is selected from zinc oxide, stearic acid, and a combination thereof. In one embodiment, a mixture of zinc oxide and stearic acid is used as the vulcanization activator. The vulcanization activator can be used in an amount ranging from 1 to 8 phr.

[0037] The cross-linkable rubber composition of the present disclosure may also include any suitable additives generally used in tire rubber compositions. In one embodiment, the cross-linkable rubber composition includes one or more additives from the group consisting of coupling agents, antioxidants, antiozonants, stabilizers, masticating agents, adhesion promoters, colorants, homogenizers, dispersion agents, and vulcanization retarders.

[0038] In one embodiment, the cross-linkable rubber composition further comprises at least one antioxidant. While any antioxidants may be used, typical antioxidants include but not limited to n-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine (6-PPD), 1,2-dihydro-2,2,4-trimethyl-quinoline (TMQ), and combination thereof. Antioxidant(s) can be used in the cross-linkable rubber composition in the range from 1 to 10 phr.

[0039] In one embodiment, the cross-linkable rubber composition further comprises at least one antiozonant. The preferred antiozonant is ozone protecting wax. Preferably, the antiozonant is present in an amount of from 0.1 to 3 phr.

[0040] In one particularly preferred embodiment, the cross-linkable rubber composition comprises 100 phr of at least one elastomer, 30 to 90 phr of a filler, 1 to 20 phr of maleated castor oil, and 0.5 to 20 phr of a vulcanization system.

[0041] In one particularly preferred embodiment, the cross-linkable rubber composition comprises 100 phr of at least one elastomer, 30 to 90 phr of a filler, 1 to 20 phr of maleated castor oil, 0.5 to 5 phr of at least one cross-linking agent, 1 to 7 phr of at least one vulcanization accelerator, and 1 to 8 phr of at least one vulcanization activator.

[0042] In one particularly preferred embodiment, the cross-linkable rubber composition comprises 100 phr of at least one elastomer, 30 to 90 phr of a filler, 1 to 20 phr of maleated castor oil, 0.5 to 5 phr of at least one cross-linking agent, 1 to 7 phr of at least one vulcanization accelerator, 1 to 8 phr of at least one vulcanization activator, 1 to 10 phr of at least one antioxidant, and 0.1 to 3 phr of at least one antiozonant.

[0043] In one exemplary embodiment, the cross-linkable rubber composition comprises:
20 phr of polybutadiene rubber (PBD),
80 phr of solution-polymerized styrene-butadiene rubber (SSBR),
70 phr of silica,

7 to 20 phr of maleated castor oil,
2 phr of sulphur,
2 phr of n-cyclohexyl-2-benzothiazole sulfenamide (CBS),
1.8 phr of diphenyl guanidine (DPG),
5 3 phr of zinc oxide,
2 phr of stearic acid,
3 phr of n-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine (6-PPD),
1 phr of 1,2-dihydro-2,2,4-trimethyl-quinoline (TMQ), and
1 phr of ozone protecting wax.

10 **[0044]** In another aspect, the present disclosure is directed to a cross-linked rubber composition, obtained by cross-linking the cross-linkable rubber composition disclosed herein. The cross-linked rubber composition can be obtained by blending the cross-linkable rubber composition with a vulcanization system and optionally with one or more additives of the type defined above to produce a blend, and heating the blend at a predetermined
15 temperature to form the cross-linked rubber composition. In one embodiment, the blend is heated to a temperature from 110° C to 200° C. In various embodiments, the cross-linked (vulcanized) rubber composition exhibits improved dispersion of filler particles, improved physical properties, improved wear resistance, and improved dynamic viscoelastic properties. In one embodiment, the cross-linked rubber composition produced according to an
20 embodiment of the present disclosure has a tan delta value in the range from ≥ 0.39 to ≤ 0.57 as measured at -20°C as per ISO 4664-1. In one embodiment, the cross-linked rubber composition produced according to an embodiment of the present disclosure has a tan delta value in the range from ≥ 0.11 to ≤ 0.15 as measured at 60°C as per ISO 4664-1. In one embodiment, the cross-linked rubber composition produced according to an embodiment of
25 the present disclosure has a tear strength in the range from 39.0 to 52.0 N/mm as determined by ASTM D 624.

[0045] In another aspect, the present disclosure is directed to a process for preparing a cross-linked rubber composition, comprising:

30 combining at least one elastomer, a filler and maleated castor oil in a mixing vessel to form a cross-linkable rubber composition;
blending the cross-linkable rubber composition with a vulcanization system and optionally with one or more additives of the type defined above to produce a blend; and heating the blend at a predetermined temperature to form the cross-linked (vulcanized) rubber composition.

[0046] In various embodiments, the cross-linkable rubber composition or the blend can be produced by mixing the above-mentioned components by using conventional kneaders used in the rubber industry, such as heating rolls, kneaders, Banbury mixers and the like. The blend can be cross-linked by heating it at temperatures ranging from 110° C to 200° C. The resultant vulcanizate (cross-linked composition) can be used for tire applications such as tire treads, under treads, carcass, side walls, and bead portions. The composition of the present disclosure can be used particularly as rubber for tire treads.

[0047] In another aspect, the present disclosure is directed to a tire or tire tread comprising the cross-linked rubber composition disclosed herein.

[0048] In another aspect, the present disclosure is directed to a finished or semifinished rubber article comprising the cross-linked rubber composition disclosed herein.

[0049] While the foregoing description discloses various embodiments of the disclosure, other and further embodiments of the invention may be devised without departing from the basic scope of the disclosure. The invention is not limited to the described embodiments, versions or examples, which are included to enable a person having ordinary skill in the art to make and use the invention when combined with information and knowledge available to the person having ordinary skill in the art.

EXAMPLES

[0050] The present disclosure is further explained in the form of following examples. However, it is to be understood that the foregoing examples are merely illustrative and are not to be taken as limitations upon the scope of the invention. Various changes and modifications to the disclosed embodiments will be apparent to those skilled in the art. Such changes and modifications may be made without departing from the scope of the invention.

Example 1: Preparation of Maleated castor oil

[0051] Maleated castor oil was prepared by reacting castor oil (CO) with maleic anhydride (MAH) in a fixed CO/MAH mole ratio of 1:3. The reaction was carried out in a three-neck flask equipped with a dean stark apparatus, a cold-water condenser, a magnetic stirrer, and a thermometer. A mixture of castor oil and xylene (at a ratio of 1:0 or 1:1 by weight) was added into the three-necked flask and heated to 140°C. Then, a portion of maleic anhydride was incrementally added to the mixture and the reaction took place for 5 h at 300 rpm. Then, xylene was removed by vacuum distillation to yield maleated castor oil. FIG. 1 depicts the reaction scheme for the preparation of maleated castor oil by reaction of castor oil with maleic anhydride. FIG. 2 shows a comparison of the FTIR spectrum of the castor oil to

the FTIR spectrum of the maleated castor oil. The maleated castor oil has characteristic FTIR peaks at 3440 cm^{-1} and 1650 cm^{-1} , as determined using ASTM E1252.

Example 2: Rubber compositions

[0052] Rubber compositions were prepared according to the ingredients and amounts indicated in Table 1. Composition production was performed under industry standard conditions in two stages, as shown in Table 2. In the first stage, the elastomers (PBD and SSBR) were added to an internal rubber mixer and mixed for about 2-5 min. Then, plasticizer oil and HD Silica were added to the mixer and the resulting composition was mixed for 2-6 min. Then, 6-PPD, TMQ, ozone protecting wax, zinc oxide and stearic acid were added to the mixer. Subsequently, all the ingredients were mixed for 8-10 min. The material was discharged from the mixer and air cooled to room temperature. In the second stage, the material from the first stage and sulfur, CBS and DPG were added into an internal rubber mixer or a two-roll open mill rubber machine and mixed for 2-6 min. The resulting composition was discharged from the mixer and air cooled. Test pieces were produced from each of the compositions by optimal vulcanization under pressure at 160° C , and these test pieces were used to determine the material properties typical for the tire industry. Testing was performed according to ASTM and ISO test methods.

Table-1

Ingredients	Composition 1	Composition 2	Composition 3
	(RAE oil)	(Castor oil)	(Maleated Castor oil)
	phr	phr	phr
PBD	20	20	20
SSBR	80	80	80
HD Silica	70	70	70
RAE oil	20	0	0
Castor Oil	0	20	0
Maleated Castor oil	0	0	20
6-PPD	3	3	3
TMQ	1	1	1
Ozone protecting wax	1	1	1
Zinc oxide	3	3	3
Stearic acid	2	2	2

CBS	2	2	2
DPG	1.8	1.8	1.8
Sulfur	2	2	2

PBD - Polybutadiene rubber

SSBR - Solution-polymerized styrene-butadiene

HD Silica - Highly dispersible silica

5 RAE oil - Residual aromatic extract oil

6-PPD - N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine

TMQ - 1,2-dihydro-2,2,4-trimethyl-quinoline

CBS - N-Cyclohexyl-2-benzothiazole sulfenamide

DPG - Diphenyl guanidine

10 Phr - Parts per hundred mass units of rubber

Table 2

First mixing step	Rotor speed (rpm) - 70 Starting temperature - 120° C Final temperature - 149° C
Second mixing step	Rotor speed (rpm) - 60 Temperature - 75° C

Curing properties

15 [0053] Curing properties of the rubber compositions were measured and are reported in Table 3.

Table 3

Parameters	Composition 1 (RAE oil)	Composition 2 (Castor oil)	Composition 3 (Maleated Castor oil)
Mooney viscosity, ML (1+4)	55	51	52
Max Torque (dNm)	22.16	20.33	17.11
Ts2 (min)	2.47	3.07	3.79
T90 (min)	14.63	20.34	15.47

[0054] As could be seen from the data shown in Table 3, the rubber composition containing maleated castor oil according to the embodiments of the present disclosure exhibits comparable cure times and better scorch times, as compared with those observed for the rubber compositions containing conventional RAE oil or unmodified castor oil as plasticizer.

5 Unaged physical properties

[0055] Unaged physical properties of the rubber compositions were measured and are reported in Table 4.

Table 4

Properties	Composition 1 (RAE oil)	Composition 2 (Castor oil)	Composition 3 (Maleated Castor oil)
Modulus @ 100% (MPa)	3.01	2.36	2.37
Modulus @ 300% (MPa)	15.49	12.21	9.99
Tensile Strength (MPa)	21.05	19.61	18.44
Elongation @ Break (%)	385	435	512
Hardness (Shore A)	70	64	71
Tear Strength (N/mm)	46.47	43.19	45.2
Rebound % @ RT	26	31	23

10 [0056] From the data shown in Table 4, it is evident that the rubber composition containing maleated castor oil shows better elongation at break and hardness than the rubber compositions containing conventional RAE oil or unmodified castor oil as plasticizer.

Aged physical properties

15 [0057] Aged physical properties of the rubber compositions were measured and are reported in Table 5.

Table 5

Properties	Composition 1 (RAE oil)	Composition 2 (Castor oil)	Composition 3 (Maleated Castor oil)
Modulus @ 100% (MPa)	4.21	3.15	3.27
Modulus @ 300% (MPa)	17.74	15.16	14.28
Tensile Strength (MPa)	21.15	16.36	16.72
Elongation @ Break (%)	313	313	351
Hardness (Shore A)	75	70	75

Tear Strength (N/mm)	42.63	36.85	43.38
Reinforcement index (M300/M100)	5.15	5.17	4.21

[0058] As is apparent from the data shown in Table 5 above, the rubber composition containing maleated castor oil shows better elongation at break and hardness than the rubber compositions containing conventional RAE oil or unmodified castor oil as plasticizer.

5 Dynamic mechanical properties

[0059] Dynamic mechanical properties of the rubber compositions were tested and the results are reported in Table 6.

Table 6

Temperature and prediction	Measurements	Composition 1 (RAE oil)	Composition 2 (Castor oil)	Composition 3 (Maleated Castor oil)
-20°C (Snow Grip)	E'(MPa)	856	716	102
	Tan delta	0.364	0.366	0.565
20°C (Dry grip)	E'(MPa)	25.9	22.8	26.9
	Tan delta	0.276	0.271	0.206
60°C (Rolling Resistance)	E'(MPa)	13.4	13.4	17.7
	Tan delta	0.127	0.15	0.146

10 **[0060]** As can be seen from the data shown in Table 6, the rubber composition containing maleated castor oil shows better snow grip with lower dynamic modulus and higher tan delta at -20°C, as compared to the composition containing conventional RAE oil (Composition 1). Further, the composition with maleated castor oil exhibits better rolling resistance with higher dynamic modulus and comparable tan delta at 60°C as compared to the composition
15 containing conventional RAE oil.

Glass transition temperature

[0061] The glass transition temperature of the rubber compositions was measured and is reported in Table 7.

Table 7

Composition	Tg (°C) Glass transition temperature	Tan delta
Composition 1 (RAE oil)	-6	0.663
Composition 2 (Castor oil)	-5.8	0.692
Composition 3 (Maleated Castor oil)	-28.5	0.648

[0062] The data contained in Table 7 show that the rubber composition containing maleated castor oil exhibits better snow grip with lower glass transition temperature compared with the rubber compositions containing conventional RAE oil or unmodified castor oil as plasticizer. Also, the composition with maleated castor oil exhibits a tan delta value at its glass transition temperature comparable to the rubber composition with conventional RAE oil and to the rubber composition with castor oil.

Example 3: Rubber compositions

[0063] Rubber compositions 4 and 5 (containing 7 phr and 10 phr of maleated castor oil, respectively) were prepared according to the ingredients and amounts indicated in Table 8. The compositions were produced using the process similar to the one in Example 2. Testing of the rubber compositions was performed according to ASTM and ISO test methods.

Table-8

Ingredients	Composition 4 (Maleated Castor oil)	Composition 5 (Maleated Castor oil)
	phr	phr
PBD	20	20
SSBR	80	80
HD Silica	70	70
Maleated Castor oil	7	10
6-PPD	3	3
TMQ	1	1
Ozone protecting wax	1	1
Zinc oxide	3	3
Stearic acid	2	2

CBS	2	2
DPG	1.8	1.8
Sulfur	2	2

Curing properties

[0064] Curing properties of the rubber composition 4 containing 7 phr of maleated castor oil were measured and compared with that of composition 1 containing 20 phr of RAE oil.

5 The results are reported in Table 9.

Table 9

Parameters	Composition 1 (20 phr of RAE oil)	Composition 4 (7 phr of Maleated Castor oil)
Mooney viscosity, ML (1+4)	55	65
Max Torque (dNm)	22.16	27.22
Ts2 (min)	2.47	1.34
T90 (min)	14.63	17.6

[0065] Table 9 shows that the rubber composition containing 7 phr of maleated castor oil according to the embodiment of the present disclosure exhibits significantly higher Mooney
10 viscosity than the conventional rubber composition (Composition 1). Also, the composition with maleated castor oil exhibits fast curing and better maximum torques compared with conventional rubber composition (Composition 1).

Unaged physical properties

[0066] Unaged physical properties of the rubber composition 4 containing 7 phr of
15 maleated castor oil were measured and compared with that of composition 1 containing 20 phr of RAE oil. The results are reported in Table 10.

Table 10

Properties	Composition 1 (20 phr of RAE oil)	Composition 4 (7 phr of Maleated Castor oil)
Modulus @ 100% (MPa)	3.01	3.18
Modulus @ 300% (MPa)	15.49	16.67
Tensile Strength (MPa)	21.05	21.19
Elongation @ Break (%)	385	368

Hardness (Shore A)	70	74
Tear Strength (N/mm)	46.47	46.31
Rebound % @ RT	26	28

[0067] The data contained in Table 10 show that the rubber composition containing 7 phr of maleated castor oil shows higher hardness than the conventional rubber composition. The composition containing 7 phr of maleated castor oil had a tensile strength, modulus, rebound and elongation at break comparable to that of the conventional rubber composition.

Aged physical properties

[0068] Aged physical properties of the rubber composition 4 containing 7 phr of maleated castor oil were measured and compared with that of composition 1 containing 20 phr of RAE oil. The results are reported in Table 11.

10

Table 11

Properties	Composition 1 (20 phr of RAE oil)	Composition 4 (7 phr of Maleated Castor oil)
Modulus @ 100% (MPa)	4.21	4.34
Modulus @ 300% (MPa)	17.74	21.5
Tensile Strength (MPa)	21.15	22.35
Elongation @ Break (%)	313	312
Hardness (Shore A)	75	79
Tear Strength (N/mm)	42.63	50.24
Reinforcement index (M300/M100)	5.15	5.24

[0069] As is evident from the data depicted in Table 11, the rubber composition containing 7 phr of maleated castor oil shows higher hardness and higher modulus at 300% than the conventional rubber composition (composition 1). Also, the composition containing 7 phr of maleated castor oil had a tensile strength, modulus at 100%, rebound and elongation at break comparable to that of the conventional rubber composition.

Dynamic mechanical properties

[0070] Dynamic mechanical properties of the rubber composition 4 containing 7 phr of maleated castor oil were measured and compared with that of composition 1 containing 20 phr of RAE oil. The results are reported in Table 12.

20

Table 12

Temperature and prediction	Measurements	Composition 1 (20 phr of RAE oil)	Composition 4 (7 phr of Maleated Castor oil)
-20°C (Snow Grip)	E'(MPa)	856	743
	Tan delta	0.364	0.39
20°C (Dry grip)	E'(MPa)	25.9	51.9
	Tan delta	0.276	0.261
60°C (Rolling Resistance)	E'(MPa)	13.4	26.8
	Tan delta	0.127	0.136

[0071] From the data shown in Table 12, it is evident that the rubber composition containing 7 phr of maleated castor oil provides better snow grip with lower dynamic modulus and higher tan delta at -20°C, as compared to composition 1 containing 20 phr of RAE oil. Also, the rubber composition containing 7 phr of maleated castor oil exhibits significant improvement in dry grip and rolling resistance properties. The rubber composition containing 7 phr of maleated castor oil when tested for dry grip at 20°C and rolling resistance at 60°C exhibited E'(MPa) and tan delta values which were double that obtained for the composition containing conventional RAE oil.

Glass transition temperature

[0072] The glass transition temperature of the rubber composition 4 containing 7 phr of maleated castor oil was measured and compared with that of composition 1 containing 20 phr of RAE oil. The results are reported in Table 13.

15

Table 13

Composition	Tg (°C) Glass transition temperature	Tan delta
Composition 1 (20 phr of RAE oil)	-6	0.663
Composition 4 (7 phr of Maleated Castor oil)	-8.3	0.552

[0073] The data contained in Table 13 show that the rubber composition containing 7 phr of maleated castor oil exhibits a glass transition temperature and a tan delta value comparable to that of the conventional rubber composition.

[0074] It is understood from the above experimental results that the performance of the rubber compositions containing unmodified castor oil as plasticizer is not suitable for tire formulations. The above examples demonstrate experimentally that the rubber compositions prepared with the chemically modified castor oil (maleated castor oil) in accordance with the present invention result in a rubber product of significantly improved properties as compared to the rubber compositions prepared with the conventional RAE oil or unmodified castor oil. In all, data from the above experiments suggest that the bio-based maleated castor oil is a suitable plasticizer for elastomers or rubbers usable in tire application and is an effective replacement of the conventional petroleum-based plasticizers like RAE oil.

We Claim:

1. A cross-linkable rubber composition, comprising:
an elastomer,
a filler, and
5 a maleated castor oil.
2. The cross-linkable rubber composition as claimed in claim 1, wherein the maleated castor oil is present in an amount of from 1 to 20 phr.
3. The cross-linkable rubber composition as claimed in claim 1, wherein the maleated castor oil has FTIR peaks at 3440 cm^{-1} and 1650 cm^{-1} .
- 10 4. The cross-linkable rubber composition as claimed in claim 1, wherein the elastomer is selected from the group consisting of natural rubber (NR), synthetic polyisoprene rubber (IR), polybutadiene rubber (PBD), polyvinyl-butadiene rubber, styrene-butadiene rubber (SBR), solution-polymerized styrene-butadiene rubber (SSBR), emulsion-polymerized styrene-butadiene rubber (ESBR), nitrile rubber (NBR), hydrogenated nitrile rubber, butyl rubber, halogenated butyl rubbers, liquid rubbers, polynorbomene copolymer, isoprene-isobutylene copolymer, chloroprene rubber, ethylene propylene diene monomer rubber (EPDM), acrylate rubber, fluorine rubber, silicone rubber, polysulfide rubber, epichlorohydrin rubber, a terpolymer formed from ethylene monomers, propylene
15 monomers, and/or ethylene propylene diene monomer (EPDM), styrene-isoprene-butadiene terpolymer, hydrated acrylonitrile butadiene rubber, isoprene-butadiene copolymer, hydrogenated styrene-butadiene rubber, butadiene acrylonitrile rubber, styrene-butadiene-styrene block copolymer (SBS), styrene-ethylene/butylene-styrene block copolymer (SEBS), styrene-[ethylene-(ethylene/propylene)]-styrene block copolymer (SEEPS), styrene-isoprene-styrene block copolymer (SIS),
20 isoprene-based block copolymers, butadiene-based block copolymers, styrenic block copolymers, hydrogenated styrenic block copolymers, styrene butadiene copolymers, polyisobutylene, ethylene vinyl acetate (EVA) polymers, polyolefins, metallocene-catalyzed polyolefin polymers and elastomers, reactor-made thermoplastic polyolefin elastomers, olefin block copolymer, polyurethane block
25 copolymer, polyamide block copolymer, thermoplastic polyolefins, thermoplastic vulcanizates, ethylene vinyl acetate copolymer, ethylene n-butyl acrylate copolymer, ethylene methyl acrylate copolymer, neoprene, urethane, ethylene
30

acrylic acid copolymer, ethylene-propylene polymers, propylene-hexene polymers, ethylene-butene polymers, ethylene octene polymers, propylene-butene polymers, ethylene-propylene-butylene terpolymers, and a mixture thereof.

- 5
5. The cross-linkable rubber composition as claimed in any of claims 1 to 4, wherein the elastomer is a blend of polybutadiene rubber with a styrene-butadiene rubber.
6. The cross-linkable rubber composition as claimed in any of claims 1 to 5, wherein the elastomer is a blend of polybutadiene rubber (PBD) with solution-polymerized styrene-butadiene (SSBR).
- 10
7. The cross-linkable rubber composition as claimed in claim 1, wherein the filler is selected from the group consisting of carbon black, silica, aluminosilicates, chalk, titanium dioxide, magnesium oxide, zinc oxide, clay, calcium carbonate, and a mixture thereof.
8. The cross-linkable rubber composition as claimed in any of claims 1 to 7, wherein the filler is present in an amount of from 30 to 90 phr.
- 15
9. The cross-linkable rubber composition as claimed in any of claims 1 to 8, wherein the filler has a BET surface of between 150 and 250 m²/g.
10. The cross-linkable rubber composition as claimed in any of claims 1 to 9, further comprising a vulcanization system.
- 20
11. The cross-linkable rubber composition as claimed in claim 10, wherein the vulcanization system is present in the cross-linkable rubber composition in an amount of from 0.5 to 20 phr.
12. The cross-linkable rubber composition as claimed in claim 10, wherein the vulcanization system comprises at least one cross-linking agent, at least one vulcanization accelerator, at least one vulcanization activator, or a mixture thereof.
- 25
13. The cross-linkable rubber composition as claimed in any of claims 1 to 12, further comprising one or more additives from the group consisting of coupling agents, antioxidants, antiozonants, stabilizers, masticating agents, adhesion promoters, colorants, homogenizers, dispersion agents, and vulcanization retarders.
- 30
14. The cross-linkable rubber composition as claimed in any of claims 1 to 13, comprising:
100 phr of at least one elastomer;
30 to 90 phr of a filler;
1 to 20 phr of maleated castor oil; and

0.5 to 20 phr of a vulcanization system.

- 15.** The cross-linkable rubber composition as claimed in any of claims 1 to 14, comprising:

100 phr of at least one elastomer;

5 30 to 90 phr of a filler;

1 to 20 phr of maleated castor oil;

0.5 to 5 phr of at least one cross-linking agent;

1 to 7 phr of at least one vulcanization accelerator; and

1 to 8 phr of at least one vulcanization activator.

- 10 **16.** The cross-linkable rubber composition as claimed in any of claims 1 to 15, comprising:

100 phr of at least one elastomer;

30 to 90 phr of a filler;

1 to 20 phr of maleated castor oil;

15 0.5 to 5 phr of at least one cross-linking agent;

1 to 7 phr of at least one vulcanization accelerator;

1 to 8 phr of at least one vulcanization activator;

1 to 10 phr of at least one antioxidant; and

0.1 to 3 phr of at least one antiozonant.

- 20 **17.** A cross-linked rubber composition, obtained by cross-linking a cross-linkable rubber composition comprising an elastomer, a filler, and a maleated castor oil.

- 18.** A process for preparing a cross-linked rubber composition, comprising:

combining at least one elastomer, a filler and a maleated castor oil to form a cross-linkable rubber composition;

25 blending the cross-linkable rubber composition with a vulcanization system and optionally with one or more additives to produce a blend; and

heating the blend at a predetermined temperature to form the cross-linked rubber composition.

- 19.** The cross-linked rubber composition as claimed in claim 17, which exhibits a tan delta value of from ≥ 0.39 to ≤ 0.57 as measured at -20°C .

- 30 **20.** The cross-linked rubber composition as claimed in claim 17, which exhibits a tan delta value of from ≥ 0.11 to ≤ 0.15 as measured at 60°C .

- 21.** The cross-linked rubber composition as claimed in claim 17, which exhibits a tear strength between 39.0 and 52.0 N/mm.

22. A tire or tire tread, comprising the cross-linked rubber composition as claimed in claim 17.
23. A finished or semifinished rubber article comprising the cross-linked rubber composition as claimed in claim 17.

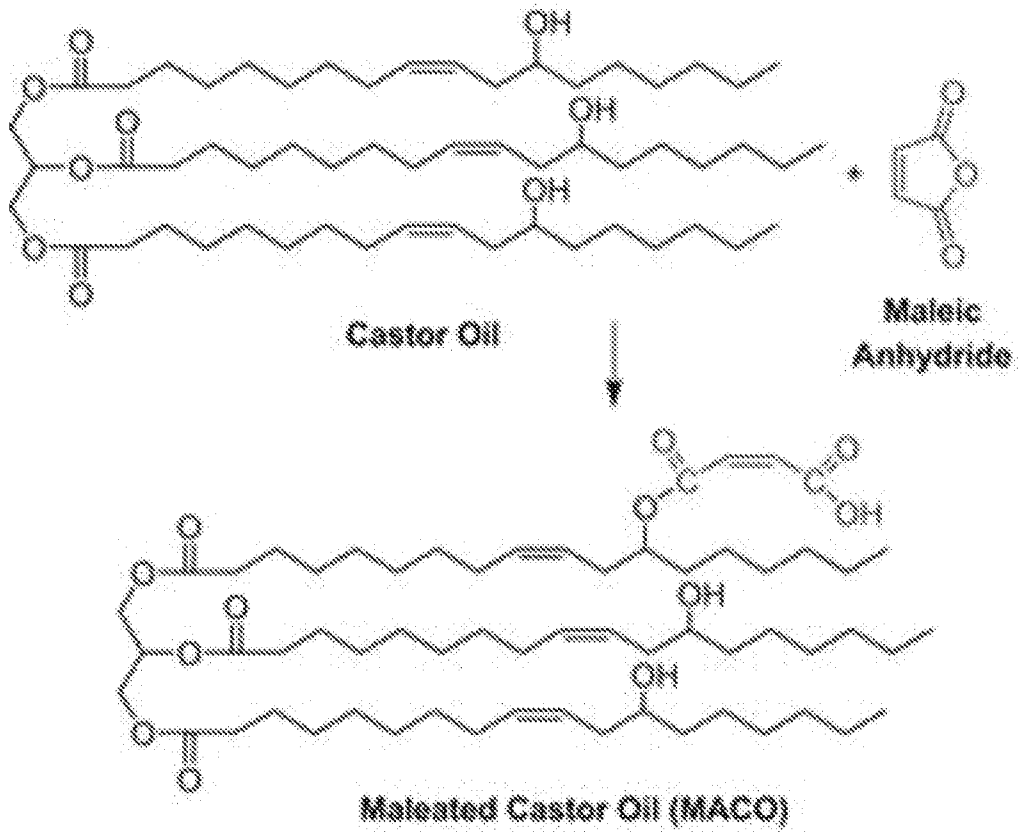


FIG. 1

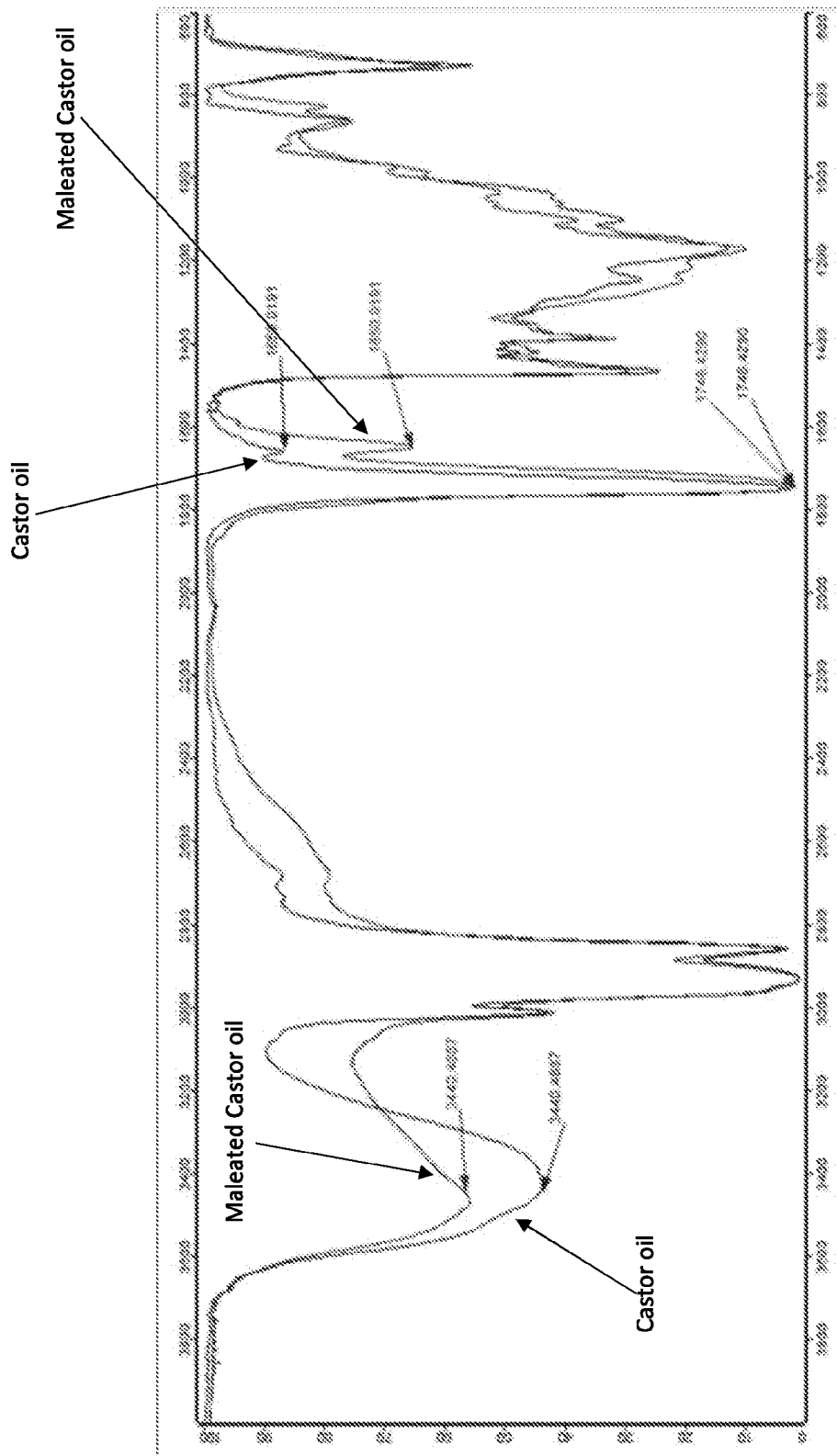


FIG. 2