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(54) Title: RUBBER VULCANIZATION PROCESSES EMPLOYING A EUTECTIC MIXTURE

(57) Abstract: A process for preparing a rubber vulcanizate, the process comprising (i) providing a vulcanizable composition of matter including a sulfur-based curative and a eutectic composition blend, where the eutectic composition blend includes a eutectic composition and an inert carrier; and (ii) heating the vulcanizable composition to thereby effect vulcanization.



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RUBBER VULCANIZATION PROCESSES EMPLOYING A EUTECTIC MIXTURE

FIELD OF THE INVENTION

[0001] Embodiments of the present invention are directed toward processes for preparing a vulcanizable composition by introducing a eutectic composition via an inert carrier.

BACKGROUND OF THE INVENTION

[0002] Zinc oxide, typically in combination with stearic acid, is commonly used in the sulfur vulcanization of rubber. It is believed that zinc species and/or zinc oxide serve as an activator for the sulfur crosslinking. It is also believed that the zinc oxide and stearic acid form, *in situ*, zinc species, and in combination with the zinc oxide, the rate and quality of the sulfur vulcanization process is impacted.

[0003] The zinc oxide conventionally employed in sulfur vulcanization processes is characterized by a BET surface area of less than 10 m²/g, which zinc oxide can be referred to as micro zinc oxide. Generally, rubber vulcanization, especially in the tire art, requires at least about 2 parts by weight (pbw) zinc oxide per 100 pbw rubber to effect a desired cure. Nano zinc oxide, which has a BET surface area greater than 10 m²/g, has also been proposed, and it has been suggested that the use of nano zinc oxide can provide improved processes that ultimately require less loading of zinc oxide or other zinc species. The use of nano zinc oxide, however, presents several difficulties including manufacturing problems as well as particle agglomeration.

[0004] There remains a desire to reduce the level of zinc, particularly zinc oxide, used in the manufacture of tire components.

SUMMARY OF THE INVENTION

[0005] One or more embodiments of the present invention provide a process for preparing a rubber vulcanizate, the process comprising (i) providing a vulcanizable composition of matter including a sulfur-based curative and a eutectic composition blend,

where the eutectic composition blend includes a eutectic composition and an inert carrier; and (ii) heating the vulcanizable composition to thereby effect vulcanization.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0006] Embodiments of the invention are based, at least in part, on the discovery of a process for preparing vulcanizable compositions including a eutectic composition. According to embodiments of the present invention, the eutectic composition is introduced in conjunction with an inert carrier. In so doing, the eutectic composition can advantageously be introduced to the composition as a blend that is a solid, which obviates the need for handling and delivering liquids. While the prior art contemplates delivery of a eutectic composition in combination with a constituent of the vulcanizable composition, such as zinc oxide, the present invention employs an inert material as the carrier. As a result, the present invention offers a mechanism whereby the eutectic composition can be delivered at variable doses to different vulcanizable compositions from a stock blend of carrier and eutectic composition without the need to vary the ingredients that would otherwise be added to the composition. According to aspects of this invention, the eutectic components can be pre-combined with inert materials and introduced to the composition as a solid blend. In particular embodiments, the inert materials include a material not conventionally included within vulcanizable compositions, particularly those used in the manufacture of tires.

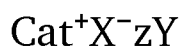
VULCANIZABLE COMPOSITIONS

[0007] As indicated above, a eutectic composition blend, which includes the combination of a eutectic composition and a carrier, is introduced to a vulcanizable composition for the production of a sulfur-cured vulcanizate. In addition to the eutectic composition blend, the vulcanizable compositions of one or more embodiments include a vulcanizable rubber, a filler, a sulfur-based curative, stearic acid, and a metal compound, such as zinc oxide or derivatives zinc oxide. Other optional ingredients may also be included such as, but not limited to, processing and/or extender oils, resins, waxes, cure accelerators, scorch inhibitors, antidegradants, antioxidants, and other rubber compounding additives known in the art.

EUTECTIC MIXTURE

[0008] In one or more embodiments, a eutectic composition includes those compositions formed by combining two or more compounds that provide a resultant combination having a melting point lower than the respective compounds that are combined. For purposes of this specification, eutectic composition may be referred to as a eutectic mixture, eutectic complex, or eutectic pair. Each of the compounds that are combined may be referred to, respectively, as a eutectic ingredient, eutectic constituent, eutectic member, or compound for forming a eutectic composition (e.g. first and second compound). Depending on the relative amounts of the respective eutectic ingredients, as well as the temperature at which the observation is made, the eutectic composition may be in the form of a liquid, which may be referred to as a eutectic liquid or eutectic solvent. For a given composition, where relative amounts of the respective ingredients are at or proximate to the lowest melting point of the eutectic mixture, then composition may be referred to as a deep eutectic solvent, which may be referred to as DES.

[0009] Without wishing to be bound by any particular theory, it is believed that the eutectic ingredients combine, otherwise react or interact to form a complex. Thus, any reference to eutectic mixture, or eutectic combination, eutectic pair, or eutectic complex will include combinations and reaction products or complexes between the constituents that are combined that yield a lower melting point than the respective constituents. For example, in one or more embodiments, useful eutectic compositions can be defined by the formula I:



where Cat^+ is a cation, X^- is a counter anion (e.g. Lewis Base), and z refers to the number of Y molecules that interact with the counter anion (e.g. Lewis or Bronsted Acid). For example, Cat^+ can include an ammonium, phosphonium, or sulfonium cation. X^- may include, for example, a halide ion. Y may include, for example, a hydrogen bond donor, a metal halide or a metal halide hydrate. In one or more embodiments, z is a number that achieves a deep eutectic solvent, or in other embodiments a number that otherwise achieves a complex having a melting point lower than the respective eutectic constituents.

[0010] In one or more embodiments, useful eutectic compositions include a combination of an acid and a base, where the acid and base may include Lewis acids and bases or Bronsted acids and bases. In one or more embodiments, useful eutectic compositions include a combination of a quaternary ammonium salt with a metal halide (which are referred to as Type I eutectic composition), a combination of a quaternary ammonium salt and a metal halide hydrate (which are referred to as Type II eutectic composition), a combination of a quaternary ammonium salt and a hydrogen bond donor (which are referred to as Type III eutectic composition), or a combination of a metal halide hydrate and a hydrogen bond donor (which are referred to as Type IV eutectic composition). Analogous combinations of sulfonium or phosphonium in lieu of ammonium compounds can also be employed and can be readily envisaged by those having skill in the art.

QUATERNARY AMMONIUM SALT

[0011] In one or more embodiments, the quaternary ammonium salt is a solid at 20 °C. In these or other embodiments, the metal halide and hydrogen bond donor are solid at 20 °C.

[0012] In one or more embodiments, useful quaternary ammonium salts, which may also be referred to as ammonium compounds, may be defined by the formula II:



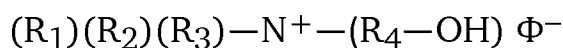
where each R_1 , R_2 , R_3 , and R_4 is individually hydrogen or a monovalent organic group, or, in the alternative, two of R_1 , R_2 , R_3 , and R_4 join to form a divalent organic group, and Φ^- is a counter anion. In one or more embodiments, at least one, in other embodiments at least two, and in other embodiments at least three of R_1 , R_2 , R_3 , and R_4 are not hydrogen.

[0013] In one or more embodiments, the counter anion (e.g. Φ^-) is selected from the group consisting of halide (X^-), nitrate (NO_3^-), tetrafluoroborate (BF_4^-), perchlorate (ClO_4^-), triflate ($SO_3CF_3^-$), trifluoroacetate ($COOCF_3^-$). In one or more embodiments, Φ^- is a halide ion, and in certain embodiments a chloride ion.

[0014] In one or more embodiments, the monovalent organic groups include hydrocarbyl groups, and the divalent organic groups include hydrocarbylene groups. In one or more embodiments, the monovalent and divalent organic groups include a heteroatom, such as, but not limited to, oxygen and nitrogen, and/or a halogen atom. Accordingly, the monovalent organic groups may include alkoxy groups, siloxy groups, ether groups, and ester groups, as well as carbonyl or acetyl substituents. In one or more embodiments, the hydrocarbyl groups and hydrocarbylene group include from 1 (or the appropriate minimum number) to about 18 carbon atoms, in other embodiments from 1 to about 12 carbon atoms, and in other embodiments from 1 to about 6 carbon atoms. The hydrocarbyl and hydrocarbylene groups may be branched, cyclic, or linear. Exemplary types of hydrocarbyl groups include alkyl, cycloalkyl, aryl and alkylaryl groups. Exemplary types of hydrocarbylene groups include alkylene, cycloalkylene, arylene, and alkylarylene groups. In particular embodiments, the hydrocarbyl groups are selected from the group consisting of methyl, ethyl, octadecyl, phenyl, and benzyl groups. In certain embodiments, the hydrocarbyl groups are methyl groups, and the hydrocarbylene groups are ethylene or propylene group.

[0015] Useful types of ammonium compounds include secondary ammonium compounds, tertiary ammonium compounds, and quaternary ammonium compounds. In these or other embodiments, the ammonium compounds include ammonium halides such as, but not limited to, ammonium chloride. In particular embodiments, the ammonium compound is a quaternary ammonium chloride. In certain embodiments, R₁, R₂, R₃, and R₄ are hydrogen, and the ammonium compound is ammonium chloride. In one or more embodiments, the ammonium compounds are asymmetric.

[0016] In one or more embodiments, the ammonium compound includes an alkoxy group and can be defined by the formula III:



where each R₁, R₂, and R₃ is individually hydrogen or a monovalent organic group, or, in the alternative, two of R₁, R₂, and R₃ join to form a divalent organic group, R₄ is a divalent

organic group, and Φ^- is a counter anion. In one or more embodiments, at least one, in other embodiments at least two, and in other embodiments at least three of R_1 , R_2 , R_3 , and are not hydrogen.

[0017] Examples of ammonium compounds defined by the formula III include, but are not limited to, N-ethyl-2-hydroxy-N,N-dimethylethanaminium chloride, 2-hydroxy-N,N,N-trimethylethanaminium chloride (which is also known as choline chloride), and N-benzyl-2-hydroxy-N,N-dimethylethanaminium chloride.

[0018] In one or more embodiments, the ammonium compound includes a halogen-containing substituent and can be defined by the formula IV:



where each R_1 , R_2 , and R_3 is individually hydrogen or a monovalent organic group, or, in the alternative, two of R_1 , R_2 , and R_3 join to form a divalent organic group, R_4 is a divalent organic group, X is a halogen atom, and Φ^- is a counter anion. In one or more embodiments, at least one, in other embodiments at least two, and in other embodiments at least three of R_1 , R_2 , R_3 , and are not hydrogen. In one or more embodiments, X is chlorine.

[0019] Examples of ammonium compounds defined by the formula III include, but are not limited to, 2-chloro-N,N,N-trimethylethanaminium (which is also referred to as chlorcholine chloride), and 2-(chlorocarbonyloxy)-N,N,N-trimethylethanaminium chloride.

HYDROGEN-BOND DONOR COMPOUNDS

[0020] In one or more embodiments, the hydrogen-bond donor compounds, which may also be referred to as HBD compounds, include, but are not limited to, amines, amides, carboxylic acids, and alcohols. In one or more embodiments, the hydrogen-bond donor compound includes a hydrocarbon chain constituent. The hydrocarbon chain constituent may include a carbon chain length including at least 2, in other embodiments at least 3, and in other embodiments at least 5 carbon atoms. In these or other embodiments, the hydrocarbon chain constituent has a carbon chain length of less than

30, in other embodiments less than 20, and in other embodiments less than 10 carbon atoms.

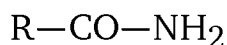
[0021] In one or more embodiments, useful amines include those compounds defined by the formula:



wherein R_1 and R_2 are $-NH_2$, $-NHR_3$, or $-NR_3R_4$, and x is an integer of at least 2. In one or more embodiments, x is from 2 to about 10, in other embodiments from about 2 to about 8, and in other embodiments from about 2 to about 6.

[0022] Specific examples of useful amines include, but are not limited to, aliphatic amines, ethylenediamine, diethylenetriamine, aminoethylpiperazine, triethylenetetramine, tris(2-aminoethyl)amine, N,N' -bis-(2-aminoethyle)piperazine, piperazinoethylethylenediamine, and tetraethylenepentaamine, propyleneamine, aniline, substituted aniline, and combinations thereof.

[0023] In one or more embodiments, useful amides include those compounds defined by the formula:



wherein R is H , NH_2 , CH_3 , or CF_3 .

[0024] Specific examples of useful amides include, but are not limited to, urea, 1-methyl urea, 1,1-dimethyl urea, 1,3-dimethylurea, thiourea, urea, benzamide, acetamide, and combinations thereof.

[0025] In one or more embodiments, useful carboxylic acids include mono-functional, di-functional, and tri-functional organic acids. These organic acids may include alkyl acids, aryl acids, and mixed alkyl-aryl acids.

[0026] Specific examples of useful mono-functional carboxylic acids include, but are not limited to, aliphatic acids, phenylpropionic acid, phenylacetic acid, benzoic acid, and combinations thereof. Specific examples of di-functional carboxylic acids include, but are not limited to, oxalic acid, malonic acid, adipic acid, succinic acid, and combinations

thereof. Specific examples of tri-functional carboxylic acids include citric acid, tricarballic acid, and combinations thereof.

[0027] Types of alcohols include, but are not limited to, monools, diols, and triols. Specific examples of monools include aliphatic alcohols, phenol, substituted phenol, and mixtures thereof. Specific examples of diols include ethylene glycol, propylene glycol, resorcinol, substituted resorcinol, and mixtures thereof. Specific examples of triols include, but are not limited to, glycerol, benzene triol, and mixtures thereof.

METAL HALIDES

[0028] Types of metal halides include, but are not limited to, chlorides, bromides, iodides and fluorides. In one or more embodiments, these metal halides include, but are not limited to, transition metal halides. The skilled person can readily envisage the corresponding metal halide hydrates.

[0029] Specific examples of useful metal halides include, but are not limited to, aluminum chloride, aluminum bromide, aluminum iodide, zinc chloride, zinc bromide, zinc iodide, tin chloride, tin bromide, tin iodide, iron chloride, iron bromide, iron iodide, and combinations thereof. The skilled person can readily envisage the corresponding metal halide hydrates. For example, aluminum chloride hexahydrate and copper chloride dihydrate correspond to the halides mentioned above.

FORMATION OF EUTECTIC COMPLEX

[0030] The skilled person can select the appropriate eutectic members at the appropriate molar ratio to provide the desired eutectic composition. The skilled person appreciates that the molar ratio of the first compound (e.g. Lewis base) of the pair to the second compound (e.g. Lewis acid) of the pair will vary based upon the compounds selected. As the skilled person will also appreciate, the melting point suppression of a eutectic solvent includes the eutectic point, which is the molar ratio of the first compound to the second compound that yields the minimum melting point suppression (i.e. deep eutectic solvent). The molar ratio of the first compound to the second compound can, however, be varied to nonetheless produce a suppression in the melting point of a eutectic solvent relative to the individual melting points of the first and second compounds that is not the minimum melting point. Practice of one or more embodiments of the present

invention therefore includes the formation a eutectic solvent at molar ratios outside of the eutectic point.

[0031] In one or more embodiments, the compounds of the eutectic pair, as well as the molar ratio of the first compound to the second compound of the pair, are selected to yield a mixture having a melting point below 130 °C, in other embodiments below 110 °C, in other embodiments below 100 °C, in other embodiments below 80 °C, in other embodiments below 60 °C, in other embodiments below 40 °C, and in other embodiments below 30 °C. In these or other embodiments, the compounds of the eutectic pair, as well as the molar ratio of the compounds, are selected to yield a mixture having a melting point above 0 °C, in other embodiments above 10 °C, in other embodiments above 20 °C, in other embodiments above 30 °C, and in other embodiments above 40 °C.

[0032] In one or more embodiments, the compounds of the eutectic pair, as well as the molar ratio of the first compound to the second compound of the pair, are selected to yield a eutectic solvent having an ability or capacity to dissolve desired metal compounds, which may be referred to as solubility or solubility power. As the skilled person will appreciate, this solubility can be quantified based upon the weight of metal compound dissolved in a given weight of eutectic solvent over a specified time at a specified temperature and pressure when saturated solutions are prepared. In one or more embodiments, the eutectic solvents of the present invention are selected to achieve a solubility for zinc oxide, over 24 hours at 50 °C under atmospheric pressure, of greater than 100 ppm, in other embodiments greater than 500 ppm, in other embodiments greater than 1000 ppm, in other embodiments greater than 1200 ppm, in other embodiments greater than 1400 ppm, and in other embodiments greater than 1600 ppm, where ppm is measured on a weight solute to weight solvent basis.

[0033] In one or more embodiments, a eutectic solvent is formed by combining the first compound with the second compound at an appropriate molar ratio to provide a solvent composition (i.e. liquid composition at the desired temperature). The mixture may be mechanically agitated by using various techniques including, but not limited to, solid state mixing or blending techniques. Generally speaking, the mixture is mixed or otherwise agitated until a liquid that is visibly homogeneous is formed. Also, the mixture

may be formed at elevated temperatures. For example, the eutectic solvent may be formed by heating the mixture to a temperature of greater than 50 °C, in other embodiments greater than 70 °C, and in other embodiments greater than 90 °C. Mixing may continue during the heating of the mixture. Once a desired mixture is formed, the eutectic solvent can be cooled to room temperature. In one or more embodiments, the cooling of the eutectic solvent may take place at a controlled rate such as at a rate of less than 1 °C/min.

[0034] In one or more embodiments, useful eutectic compositions can be obtained commercially. For example, deep eutectic solvents are commercially available under the tradenames Ionic Liquids from Scionix. Useful eutectic compositions are also generally known as described in U.S. Publ. Nos. 2004/0097755 A1 and 2011/0207633 A1, which are incorporated herein by reference.

INERT CARRIER

[0035] In one or more embodiments, the inert carrier, which may also be referred to as inert material, is a solid, particulate material that does not react with or otherwise have an appreciable impact on any other constituents of the vulcanizable composition. Examples of useful inert materials that may be used in the formation of the eutectic composition include, for example, calcium carbonate (CaCO₃), wollastonite (CaSiO₃), silicon dioxide (SiO₂), and a mixture of two or more thereof. In one more embodiments, the inert carrier is devoid of or substantially devoid of zinc oxide. In these or other embodiments, the inert carrier is devoid of or substantially devoid of magnesium oxide. In these or other embodiments, the inert carrier is devoid of any metal oxide.

[0036] In one or more embodiments, the inert material is a particulate material characterized by a primary particle size median diameter (d₅₀) of less than 200 nm, in other embodiments less than 150 nm, and in other embodiments less than 100 nm.

VULCANIZABLE RUBBER

[0037] In one or more embodiments, the vulcanizable rubber, which may also be referred to as a rubber or a vulcanizable elastomer, may include those polymers that can be vulcanized to form compositions possessing rubbery or elastomeric properties. These elastomers may include natural and synthetic rubbers. The synthetic rubbers typically derive from the polymerization of conjugated diene monomer, the copolymerization of

conjugated diene monomer with other monomer such as vinyl-substituted aromatic monomer, or the copolymerization of ethylene with one or more α -olefins and optionally one or more diene monomers.

[0038] Exemplary elastomers include natural rubber, synthetic polyisoprene, polybutadiene, polyisobutylene-co-isoprene, neoprene, poly(ethylene-co-propylene), poly(styrene-co-butadiene), poly(styrene-co-isoprene), poly(styrene-co-isoprene-co-butadiene), poly(isoprene-co-butadiene), poly(ethylene-co-propylene-co-diene), polysulfide rubber, acrylic rubber, urethane rubber, silicone rubber, epichlorohydrin rubber, and mixtures thereof. These elastomers can have a myriad of macromolecular structures including linear, branched, and star-shaped structures. These elastomers may also include one or more functional units, which typically include heteroatoms.

FILLER

[0039] As suggested above, the vulcanizable compositions of the invention may include one or more fillers. These filler materials may include reinforcing and non-reinforcing fillers. Exemplary fillers include carbon black, silica, and sundry inorganic fillers.

[0040] Useful carbon blacks include furnace blacks, channel blacks, and lamp blacks. More specific examples of carbon blacks include super abrasion furnace blacks, intermediate super abrasion furnace blacks, high abrasion furnace blacks, fast extrusion furnace blacks, fine furnace blacks, semi-reinforcing furnace blacks, medium processing channel blacks, hard processing channel blacks, conducting channel blacks, and acetylene blacks.

[0041] In particular embodiments, the carbon blacks may have a surface area (EMSA) of at least 20 m²/g and in other embodiments at least 35 m²/g; surface area values can be determined by ASTM D-1765 using the cetyltrimethylammonium bromide (CTAB) technique. The carbon blacks may be in a pelletized form or an unpelletized flocculent form. The preferred form of carbon black may depend upon the type of mixing equipment used to mix the rubber compound.

[0042] Examples of suitable silica fillers include precipitated amorphous silica, wet silica (hydrated silicic acid), dry silica (anhydrous silicic acid), fumed silica, calcium silicate, aluminum silicate, magnesium silicate, and the like.

[0043] In one or more embodiments, silicas may be characterized by their surface areas, which give a measure of their reinforcing character. The Brunauer, Emmet and Teller (“BET”) method (described in *J. Am. Chem. Soc.*, vol. 60, p. 309 et seq.) is a recognized method for determining the surface area. The BET surface area of silica is generally less than 450 m²/g. Useful ranges of surface area include from about 32 to about 400 m²/g, about 100 to about 250 m²/g, and about 150 to about 220 m²/g.

[0044] Where one or more silicas is employed, the pH’s of the silicas are generally from about 5 to about 7 or slightly over 7, or in other embodiments from about 5.5 to about 6.8.

[0045] In one or more embodiments, where silica is employed as a filler (alone or in combination with other fillers), a coupling agent and/or a shielding agent may be added to the rubber compositions during mixing in order to enhance the interaction of silica with the elastomers. Useful coupling agents and shielding agents are disclosed in U.S. Patent Nos. 3,842,111, 3,873,489, 3,978,103, 3,997,581, 4,002,594, 5,580,919, 5,583,245, 5,663,396, 5,674,932, 5,684,171, 5,684,172, 5,696,197, 6,608,145, 6,667,362, 6,579,949, 6,590,017, 6,525,118, 6,342,552, and 6,683,135, which are incorporated herein by reference. Examples of sulfur-containing silica coupling agents include bis(trialkoxysilylorgano)polysulfides or mercapto-organoalkoxysilanes. Types of bis(trialkoxysilylorgano)polysulfides include bis(trialkoxysilylorgano)disulfide and bis(trialkoxysilylorgano)tetrasulfides.

[0046] Other useful filler materials include sundry inorganic and organic fillers. Examples of organic fillers include starch. Examples of inorganic fillers include silica, aluminum hydroxide, magnesium hydroxide, titanium oxides, boron nitrides, iron oxides, mica, talc (hydrated magnesium silicate), and clays (hydrated aluminum silicates).

RESINS

[0047] As suggested above, the vulcanizable compositions of the invention may include one or more resins. These resins may include phenolic resins and hydrocarbon resins such as cycloaliphatic resins, aliphatic resins, aromatic resins, terpene resins, and combinations thereof. Useful resins are commercially available from various companies including, for example, Chemfax, Dow Chemical Company, Eastman Chemical Company,

Idemitsu, Neville Chemical Company, Nippon, Polysat Inc., Resinall Corp., Pinova Inc., Yasuhara Chemical Co., Ltd., Arizona Chemical, and SI Group Inc., and Zeon under various trade names.

[0048] In one or more embodiments, useful hydrocarbon resins may be characterized by a glass transition temperature (T_g) of from about 30 to about 160 °C, in other embodiments from about 35 to about 60 °C, and in other embodiments from about 70 to about 110 °C. In one or more embodiments, useful hydrocarbon resins may also be characterized by its softening point being higher than its T_g. In certain embodiments, useful hydrocarbon resins have a softening point of from about 70 to about 160 °C, in other embodiments from about 75 to about 120 °C, and in other embodiments from about 120 to about 160 °C.

[0049] In certain embodiments, one or more cycloaliphatic resins are used in combination with one or more of an aliphatic, aromatic, and terpene resins. In one or more embodiments, one or more cycloaliphatic resins are employed as the major weight component (e.g. greater than 50% by weight) relative to total load of resin. For example, the resins employed include at least 55% by weight, in other embodiments at least 80% by weight, and in other embodiments at least 99% by weight of one or more cycloaliphatic resins.

[0050] In one or more embodiments, cycloaliphatic resins include both cycloaliphatic homopolymer resins and cycloaliphatic copolymer resins including those deriving from cycloaliphatic monomers, optionally in combination with one or more other (non-cycloaliphatic) monomers, with the majority by weight of all monomers being cycloaliphatic. Non-limiting examples of useful cycloaliphatic resins suitable include cyclopentadiene (“CPD”) homopolymer or copolymer resins, dicyclopentadiene (“DCPD”) homopolymer or copolymer resins, and combinations thereof. Non-limiting examples of cycloaliphatic copolymer resins include CPD/vinyl aromatic copolymer resins, DCPD/vinyl aromatic copolymer resins, CPD/terpene copolymer resins, DCPD/terpene copolymer resins, CPD/aliphatic copolymer resins (e.g., CPD/C5 fraction copolymer resins), DCPD/aliphatic copolymer resins (e.g., DCPD/C5 fraction copolymer resins), CPD/aromatic copolymer resins (e.g., CPD/C9 fraction copolymer resins), DCPD/aromatic

copolymer resins (e.g., DCPD/C9 fraction copolymer resins), CPD/aromatic-aliphatic copolymer resins (e.g., CPD/C5 & C9 fraction copolymer resins), DCPD/aromatic-aliphatic copolymer resins (e.g., DCPD/C5 & C9 fraction copolymer resins), CPD/vinyl aromatic copolymer resins (e.g., CPD/styrene copolymer resins), DCPD/vinyl aromatic copolymer resins (e.g., DCPD/styrene copolymer resins), CPD/terpene copolymer resins (e.g., limonene/CPD copolymer resin), and DCPD/terpene copolymer resins (e.g., limonene/DCPD copolymer resins). In certain embodiments, the cycloaliphatic resin may include a hydrogenated form of one of the cycloaliphatic resins discussed above (i.e., a hydrogenated cycloaliphatic resin). In other embodiments, the cycloaliphatic resin excludes any hydrogenated cycloaliphatic resin; in other words, the cycloaliphatic resin is not hydrogenated.

[0051] In certain embodiments, one or more aromatic resins are used in combination with one or more of an aliphatic, cycloaliphatic, and terpene resins. In one or more embodiments, one or more aromatic resins are employed as the major weight component (e.g. greater than 50% by weight) relative to total load of resin. For example, the resins employed include at least 55% by weight, in other embodiments at least 80% by weight, and in other embodiments at least 99% by weight of one or more aromatic resins.

[0052] In one or more embodiments, aromatic resins include both aromatic homopolymer resins and aromatic copolymer resins including those deriving from one or more aromatic monomers in combination with one or more other (non-aromatic) monomers, with the largest amount of any type of monomer being aromatic. Non-limiting examples of useful aromatic resins include coumarone-indene resins and alkyl-phenol resins, as well as vinyl aromatic homopolymer or copolymer resins, such as those deriving from one or more of the following monomers: alpha-methylstyrene, styrene, ortho-methylstyrene, meta-methylstyrene, para-methylstyrene, vinyltoluene, para(tert-butyl)styrene, methoxystyrene, chlorostyrene, hydroxystyrene, vinylmesitylene, divinylbenzene, vinylnaphthalene or any vinyl aromatic monomer resulting from C9 fraction or C8-C10 fraction. Non-limiting examples of vinylaromatic copolymer resins include vinylaromatic/terpene copolymer resins (e.g., limonene/styrene copolymer resins), vinylaromatic/C5 fraction resins (e.g., C5 fraction/styrene copolymer resin),

vinylaromatic/aliphatic copolymer resins (e.g., CPD/styrene copolymer resin, and DCPD/styrene copolymer resin). Non-limiting examples of alkyl-phenol resins include alkylphenol-acetylene resins such as p-tert-butylphenol-acetylene resins, alkylphenol-formaldehyde resins (such as those having a low degree of polymerization. In certain embodiments, the aromatic resin may include a hydrogenated form of one of the aromatic resins discussed above (i.e., a hydrogenated aromatic resin). In other embodiments, the aromatic resin excludes any hydrogenated aromatic resin; in other words, the aromatic resin is not hydrogenated.

[0053] In certain embodiments, one or more aliphatic resins are used in combination with one or more of cycloaliphatic, aromatic and terpene resins. In one or more embodiments, one or more aliphatic resins are employed as the major weight component (e.g. greater than 50% by weight) relative to total load of resin. For example, the resins employed include at least 55% by weight, in other embodiments at least 80% by weight, and in other embodiments at least 99% by weight of one or more aliphatic resins.

[0054] In one or more embodiments, aliphatic resins include both aliphatic homopolymer resins and aliphatic copolymer resins including those deriving from one or more aliphatic monomers in combination with one or more other (non-aliphatic) monomers, with the largest amount of any type of monomer being aliphatic. Non-limiting examples of useful aliphatic resins include C5 fraction homopolymer or copolymer resins, C5 fraction/C9 fraction copolymer resins, C5 fraction/vinyl aromatic copolymer resins (e.g., C5 fraction/styrene copolymer resin), C5 fraction/cycloaliphatic copolymer resins, C5 fraction/C9 fraction/cycloaliphatic copolymer resins, and combinations thereof. Non-limiting examples of cycloaliphatic monomers include, but are not limited to cyclopentadiene (“CPD”) and dicyclopentadiene (“DCPD”). In certain embodiments, the aliphatic resin may include a hydrogenated form of one of the aliphatic resins discussed above (i.e., a hydrogenated aliphatic resin). In other embodiments, the aliphatic resin excludes any hydrogenated aliphatic resin; in other words, in such embodiments, the aliphatic resin is not hydrogenated.

[0055] In one or more embodiments, terpene resins include both terpene homopolymer resins and terpene copolymer resins including those deriving from one or

more terpene monomers in combination with one or more other (non-terpene) monomers, with the largest amount of any type of monomer being terpene. Non-limiting examples of useful terpene resins include alpha-pinene resins, beta-pinene resins, limonene resins (e.g., L-limonene, D-limonene, dipentene which is a racemic mixture of L- and D-isomers), beta-phellandrene, delta-3-carene, delta-2-carene, pinene-limonene copolymer resins, terpene-phenol resins, aromatic modified terpene resins and combinations thereof. In certain embodiments, the terpene resin may include a hydrogenated form of one of the terpene resins discussed above (i.e., a hydrogenated terpene resin). In other embodiments, the terpene resin excludes any hydrogenated terpene resin; in other words, in such embodiments, the terpene resin is not hydrogenated.

CURATIVES

[0056] The rubber curing agents (also called vulcanizing agents) include sulfur-based curing systems. Curing agents are described in *Kirk-Othmer, ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY*, Vol. 20, pgs. 365-468, (3rd Ed. 1982), particularly *Vulcanization Agents and Auxiliary Materials*, pgs. 390-402, and A.Y. Coran, *Vulcanization, ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING*, (2nd Ed. 1989), which are incorporated herein by reference. In one or more embodiments, the curative is sulfur. Examples of suitable sulfur vulcanizing agents include “rubbermaker's” soluble sulfur; sulfur donating vulcanizing agents, such as an amine disulfide, polymeric polysulfide or sulfur olefin adducts; and insoluble polymeric sulfur. Vulcanizing agents may be used alone or in combination. The skilled person will be able to readily select the amount of vulcanizing agents to achieve the level of desired cure.

[0057] In one or more embodiments, the curative is employed in combination with a cure accelerator. In one or more embodiments, accelerators are used to control the time and/or temperature required for vulcanization and to improve properties of the vulcanizate. Examples of accelerators include thiazole vulcanization accelerators, such as 2-mercaptobenzothiazole, dibenzothiazyl disulfide, N-cyclohexyl-2-benzothiazyl-sulfenamide (CBS), and the like, and guanidine vulcanization accelerators, such as diphenylguanidine (DPG) and the like. The skilled person will be able to readily select the amount of cure accelerators to achieve the level of desired cure.

OTHER INGREDIENTS

[0058] Other ingredients that are typically employed in rubber compounding may also be added to the rubber compositions. These include accelerators, accelerator activators, oils, additional plasticizers, waxes, scorch inhibiting agents, processing aids, zinc oxide, tackifying resins, reinforcing resins, fatty acids such as stearic acid, peptizers, and antidegradants such as antioxidants and antiozonants. In particular embodiments, the oils that are employed include those conventionally used as extender oils. Useful oils or extenders that may be employed include, but are not limited to, aromatic oils, paraffinic oils, naphthenic oils, vegetable oils other than castor oils, low PCA oils including MES, TDAE, and SRAE, and heavy naphthenic oils. Suitable low PCA oils also include various plant-sourced oils such as can be harvested from vegetables, nuts, and seeds. Non-limiting examples include, but are not limited to, soy or soybean oil, sunflower oil, safflower oil, corn oil, linseed oil, cotton seed oil, rapeseed oil, hemp oil, cashew oil, sesame oil, camellia oil, jojoba oil, macadamia nut oil, coconut oil, and palm oil.

METAL ACTIVATOR AND ORGANIC ACID

[0059] As suggested above, the vulcanizable compositions of the present invention include a metal compound. In one or more embodiments, the metal compound is an activator (i.e. assists in the vulcanization or cure of the rubber). In other embodiments, the metal activator is a metal oxide. In particular embodiments, the metal activator is zinc oxide. In other embodiments, the metal activator is a zinc species that is formed *in situ* through a reaction or interaction between zinc oxide and organic acid (e.g. stearic acid). In other embodiments, the metal compound is a magnesium compound such as magnesium hydroxide. In other embodiments, the metal compound is an iron compound such as an iron oxide. In other embodiments, the metal compound is a cobalt compound such as a cobalt carboxylate.

[0060] In one or more embodiments, the zinc oxide is an unfunctionalized zinc oxide characterized by a BET surface area of less than 10 m²/g, in other embodiments less than 9 m²/g, and in other embodiments less than 8 m²/g. In other embodiments, nano zinc oxide is employed, which includes those zinc oxide particles that are characterized by a BET surface area of greater than 10 m²/g.

[0061] In one or more embodiments, the organic acid is a carboxylic acid. In particular embodiments, the carboxylic acid is a fatty acid including saturated and unsaturated fatty acids. In particular embodiments, saturated fatty acids, such as stearic acid, are employed. Other useful acids include, but are not limited to, palmitic acid, arachidic acid, oleic acid, linoleic acid, and arachidonic acid.

INGREDIENT AMOUNTS

RUBBER

[0062] In one or more embodiments, the vulcanizable compositions include at least 20, in other embodiments at least 30, and in other embodiments at least 40 percent by weight of the rubber component, based upon the entire weight of the composition. In these or other embodiments, the vulcanizable compositions include at most 90, in other embodiments at most 70, and in other embodiments at most 60 percent by weight of the rubber component based on the entire weight of the composition. In one or more embodiments, the vulcanizable compositions include from about 20 to about 90, in other embodiments from about 30 to about 70, and in other embodiments from about 40 to about 60 percent by weight of the rubber component based upon the entire weight of the composition.

EUTECTIC COMPOSITION

[0063] In one or more embodiments, the vulcanizable compositions include greater than 0.005, in other embodiments greater than 0.01, and in other embodiments greater than 0.02 parts by weight (pbw) of the eutectic composition per 100 parts by weight rubber (phr). In these or other embodiments, the vulcanizable compositions include less than 3, in other embodiments less than 1, and in other embodiments less than 0.1 pbw of the eutectic composition phr. In one or more embodiments, the vulcanizable compositions include from about 0.005 to about 3, in other embodiments from about 0.01 to about 1, and in other embodiments from about 0.02 to about 0.1 pbw of the eutectic composition phr.

[0064] In one or more embodiments, the amount of eutectic solvent can be described with reference to the loading of metal activator (such as zinc oxide). In one or more embodiments, the vulcanizable compositions include greater than 2, in other embodiments greater than 3, and in other embodiments greater than 5 wt % eutectic solvent based upon

the total weight of the eutectic solvent and the metal activator (e.g. zinc oxide) present within the vulcanizable composition. In these or other embodiments, the vulcanizable compositions include less than 15, in other embodiments less than 12, and in other embodiments less than 10 wt % eutectic solvent based upon the total weight of the eutectic solvent and the metal activator (e.g. zinc oxide) present within the vulcanizable composition. In one or more embodiments, the vulcanizable compositions include from about 2 to about 15, in other embodiments from about 3 to about 12, and in other embodiments from about 5 to about 10 wt % eutectic solvent based upon the total weight of the eutectic solvent and the metal activator (e.g. zinc oxide) present within the vulcanizable composition.

CARRIER MATERIAL

[0065] In one or more embodiments, the amount of carrier material introduced in conjunction with the eutectic composition (i.e. the eutectic composition blend) can be described relative to the weight of the eutectic composition. In one or more embodiments, the weight ratio of eutectic composition to carrier is greater than 0.05:1, in other embodiments greater than 0.01:1, and in other embodiments greater than 0.2:1. In these or other embodiments, the weight ratio of the eutectic composition to the carrier is less than 5:1, in other embodiments less than 3:1, and in other embodiments less than 1:1. In one or more embodiments, the weight ratio of the eutectic composition to the carrier is from about 0.05:1 to about 5:1, in other embodiments from about 0.1:1 to about 3:1, and in other embodiments from about 0.2:1 to about 1:1.

METAL COMPOUND

[0066] In one or more embodiments, the vulcanizable compositions include greater than 0.05, in other embodiments greater than 0.1, and in other embodiments greater than 0.15 parts by weight (pbw) of metal activator (e.g. zinc oxide) per 100 parts by weight rubber (phr). In these or other embodiments, the vulcanizable composition includes less than 2, in other embodiments less than 1, and in other embodiments less than 0.75 pbw of metal activator (e.g. zinc oxide) phr. In one or more embodiments, the vulcanizable composition includes from about 0.05 to about 2, in other embodiments from about 0.1

to about 1, and in other embodiments from about 0.15 to about 0.75 pbw of metal activator (e.g. zinc oxide) phr.

ORGANIC ACID

[0067] In one or more embodiments, the vulcanizable compositions include greater than 0.5, in other embodiments greater than 0.7, and in other embodiments greater than 1.0 parts by weight (pbw) of organic acid (e.g. stearic acid) per 100 parts by weight rubber (phr). In these or other embodiments, the vulcanizable composition includes less than 5, in other embodiments less than 3, and in other embodiments less than 2 pbw of organic acid (e.g. stearic acid) phr. In one or more embodiments, the vulcanizable composition includes from about 0.5 to about 5, in other embodiments from about 0.7 to about 3, and in other embodiments from about 1.0 to about 2 pbw of organic acid (e.g. stearic acid) phr.

FILLER

[0068] In one or more embodiments, the vulcanizable compositions include at least 0, in other embodiments at least 10, and in other embodiments at least 20 parts by weight (pbw) of filler per 100 parts by weight rubber (phr). In these or other embodiments, the vulcanizable composition includes at most 200, in other embodiments at most 100, and in other embodiments at most 70 pbw of filler phr. In one or more embodiments, the vulcanizable composition includes from about 0 to about 200, in other embodiments from about 10 to about 100, and in other embodiments from about 20 to about 70 pbw of filler phr.

CARBON BLACK

[0069] In one or more embodiments, the vulcanizable compositions include at least 0, in other embodiments at least 10, and in other embodiments at least 20 parts by weight (pbw) of a carbon black per 100 parts by weight rubber (phr). In these or other embodiments, the vulcanizable composition includes at most 200, in other embodiments at most 100, and in other embodiments at most 70 pbw of a carbon black phr. In one or more embodiments, the vulcanizable composition includes from about 0 to about 200, in other embodiments from about 10 to about 100, and in other embodiments from about 20 to about 70 pbw of a carbon black phr.

SILICA

[0070] In one or more embodiments, the vulcanizable compositions include at least 5, in other embodiments at least 25, in other embodiments at least 50, and in other embodiments at least 70 parts by weight (pbw) silica per 100 parts by weight rubber (phr). In these or other embodiments, the vulcanizable composition includes at most 200, in other embodiments at most 130, and in other embodiments at most 80 pbw of the silica phr. In one or more embodiments, the vulcanizable composition includes from about 5 to about 200, in other embodiments from about 25 to about 130, and in other embodiments from about 50 to about 80 pbw of silica phr.

FILLER RATIO

[0071] In one or more embodiments, the vulcanizable compositions can be characterized by the ratio of the amount of a first filler to the amount of a second filler. In one or more embodiments, the ratio of the amount of carbon black to silica is about 1:1, in other embodiments about 10:1, in other embodiments about 14:1, and in other embodiments about 20:1. In one or more embodiments, the ratio of the amount of carbon black to silica is about 1:5, in other embodiments about 1:10, in other embodiments about 1:14, and in other embodiments about 1:20.

SILICA COUPLING AGENT

[0072] In one or more embodiments, the vulcanizable compositions include at least 1, in other embodiments at least 2, and in other embodiments at least 5 parts by weight (pbw) silica coupling agent per 100 parts by weight silica. In these or other embodiments, the vulcanizable composition includes at most 20, in other embodiments at most 15, and in other embodiments at most 10 pbw of the silica coupling agent per 100 parts by weight silica. In one or more embodiments, the vulcanizable composition includes from about 1 to about 20, in other embodiments from about 2 to about 15, and in other embodiments from about 5 to about 10 pbw of silica coupling agent per 100 parts by weight silica.

RESIN

[0073] In one or more embodiments, the vulcanizable compositions include greater than 1, in other embodiments greater than 15, in other embodiments greater than 25, and in other embodiments greater than 35 parts by weight (pbw) of resin (e.g. hydrocarbon

resin) per 100 parts by weight rubber (phr). In these or other embodiments, the vulcanizable composition includes less than 150, in other embodiments less than 120, and in other embodiments less than 90 pbw of resin (e.g. hydrocarbon resin) phr. In one or more embodiments, the vulcanizable composition includes from about 1 to about 150, in other embodiments from about 15 to about 120, and in other embodiments from about 25 to about 90 pbw of resin (e.g. hydrocarbon resin) phr.

PROCESS OVERVIEW

[0074] According to aspects of the invention, the eutectic composition is pre-combined with the inert carrier to form the eutectic composition blend. This blend is then added to the vulcanizable compositions. In one or more embodiments, the eutectic composition is prepared prior to combining the eutectic composition with the carrier. In other embodiments, the constituents of the eutectic composition (i.e. the eutectic ingredients) are introduced in the presence of the inert carrier. In other words, each of the eutectic constituents are introduced directly and separately with the inert carrier.

[0075] In one or more embodiments, vulcanizable compositions are prepared by mixing a vulcanizable rubber and the eutectic composition blend to form a masterbatch, and then subsequently adding a curative to the masterbatch. The preparation of the masterbatch may take place using one or more sub-mixing steps where, for example, one or more ingredients may be added to the composition sequentially after an initial mixture is prepared by mixing two or more ingredients. Also, using conventional technology, additional ingredients can be added in the preparation of the vulcanizable compositions such as, but not limited to, carbon black, additional fillers, chemically-treated inorganic oxide, silica, silica coupling agent, silica dispersing agent, processing oils, processing aids such as zinc oxide and fatty acid, and antidegradants such as antioxidants or antiozonants.

[0076] In one or more embodiments, the eutectic composition blend is introduced to the vulcanizable rubber as an initial ingredient in the formation of a rubber masterbatch. As a result, the eutectic composition blend undergoes high shear, high temperature mixing with the rubber. In one or more embodiments, the eutectic composition blend undergoes mixing with the rubber at minimum temperatures in excess of 110 °C, in other embodiments in excess of 130 °C, and in other embodiments in excess of 150 °C. In one

or more embodiments, high shear, high temperature mixing takes place at a temperature from about 110 °C to about 170 °C.

[0077] In other embodiments, the eutectic composition blend is introduced to the vulcanizable rubber, either sequentially or simultaneously, with the sulfur-based curative. As a result, the eutectic composition blend undergoes mixing with the vulcanizable rubber at a maximum temperature below 110 °C, in other embodiments below 105 °C, and in other embodiments below 100 °C. In one or more embodiments, mixing with the curative takes place at a temperature from about 70 °C to about 110 °C.

[0078] As with the eutectic composition blend, the zinc oxide and the stearic acid can be added as initial ingredients to the rubber masterbatch, and therefore these ingredients will undergo high temperature, high shear mixing. Alternatively, the zinc oxide and the stearic acid can be added along with the sulfur-based curative and thereby only undergo low-temperature mixing.

[0079] In one or more embodiments, the zinc oxide is introduced to the vulcanizable rubber separately and individually from the eutectic composition blend. In other embodiments, the zinc oxide and the eutectic composition blend are pre-combined to form a zinc oxide masterbatch, which may include a solution in which the zinc oxide is dissolved or otherwise dispersed in the eutectic composition blend. The zinc oxide masterbatch can then be introduced to the vulcanizable rubber.

MIXING CONDITIONS

[0080] In one or more embodiments, a vulcanizable composition is prepared by first mixing a vulcanizable rubber and the eutectic composition blend at a temperature of from about 140 to about 180, or in other embodiments from about 150 to about 170 °C. In certain embodiments, following the initial mixing, the composition (i.e., masterbatch) is cooled to a temperature of less than 100 °C, or in other embodiments less than 80 °C, and a curative is added. In certain embodiments, mixing is continued at a temperature of from about 90 to about 110 °C, or in other embodiments from about 95 to about 105 °C, to prepare the final vulcanizable composition.

[0081] In one or more embodiments, the masterbatch mixing step, or one or more sub-steps of the masterbatch mixing step, may be characterized by the peak temperature

obtained by the composition during the mixing. This peak temperature may also be referred to as a drop temperature. In one or more embodiments, the peak temperature of the composition during the masterbatch mixing step may be at least 140 °C, in other embodiments at least 150 °C, and in other embodiments at least 160 °C. In these or other embodiments, the peak temperature of the composition during the masterbatch mixing step may be from about 140 to about 200 °C, in other embodiments from about 150 to about 190 °C, and in other embodiments from about 160 to about 180 °C.

FINAL MIXING STEP

[0082] Following the masterbatch mixing step, a curative or curative system is introduced to the composition and mixing is continued to ultimately form the vulcanizable composition of matter. This mixing step may be referred to as the final mixing step, the curative mixing step, or the productive mixing step. The resultant product from this mixing step may be referred to as the vulcanizable composition.

[0083] In one or more embodiments, the final mixing step may be characterized by the peak temperature obtained by the composition during final mixing. As the skilled person will recognize, this temperature may also be referred to as the final drop temperature. In one or more embodiments, the peak temperature of the composition during final mixing may be at most 130 °C, in other embodiments at most 110 °C, and in other embodiments at most 100 °C. In these or other embodiments, the peak temperature of the composition during final mixing may be from about 80 to about 130 °C, in other embodiments from about 90 to about 115 °C, and in other embodiments from about 95 to about 105 °C.

MIXING EQUIPMENT

[0084] All ingredients of the vulcanizable compositions can be mixed with standard mixing equipment such as internal mixers (e.g. Banbury or Brabender mixers), extruders, kneaders, and two-rolled mills. Mixing can take place singularly or in tandem. As suggested above, the ingredients can be mixed in a single stage, or in other embodiments in two or more stages. For example, in a first stage (i.e., mixing stage), which typically includes the rubber component and filler, a masterbatch is prepared. Once the masterbatch is prepared, the vulcanizing agents may be introduced and mixed into the

masterbatch in a final mixing stage, which is typically conducted at relatively low temperatures so as to reduce the chances of premature vulcanization. Additional mixing stages, sometimes called remills, can be employed between the masterbatch mixing stage and the final mixing stage.

PREPARATION OF TIRE

[0085] The vulcanizable compositions can be processed into tire components according to ordinary tire manufacturing techniques including standard rubber shaping, molding and curing techniques. Typically, vulcanization is effected by heating the vulcanizable composition in a mold; e.g., it may be heated to about 140 °C to about 180 °C. Cured or crosslinked rubber compositions may be referred to as vulcanizates, which generally contain three-dimensional polymeric networks that are thermoset. The other ingredients, such as fillers and processing aids, may be evenly dispersed throughout the crosslinked network. Pneumatic tires can be made as discussed in U.S. Patent Nos. 5,866,171, 5,876,527, 5,931,211, and 5,971,046, which are incorporated herein by reference.

VULCANIZATE CHARACTERISTICS

[0086] As indicated above, the vulcanizable compositions of the present invention can be cured to prepare various tire components. These tire components include, without limitation, tire treads, tire sidewalls, belt skims, innerliners, and bead apex.

[0087] According to aspects of the present invention, the tire components, which may also be referred to as vulcanizates, are characterized by advantageous cure characteristics while including relatively low levels of metal activator such as zinc species.

[0088] In one or more embodiments, the vulcanizates are characterized by including less than 2 pbw, in other embodiments less than 1 phr, and in other embodiments less than 0.7 pbw zinc per 100 pbw rubber.

[0089] In one or more embodiments, the tire component is a tire tread. While only including the limited levels of metal activator, such as zinc species, as outlined in this specification, the treads nonetheless are characterized by a 300% modulus of greater than 3 MPa, in other embodiments greater than 5 MPa, and in other embodiments greater than 7 MPa, as determined by ASTM D-412 at room temperature.

[0090] In order to demonstrate the practice of the present invention, the following examples have been prepared and tested. The examples should not, however, be viewed as limiting the scope of the invention. The claims will serve to define the invention.

EXAMPLES

[0091] Several vulcanizable compositions were prepared by using the ingredients and mixing order provided in the Tables below. All amounts are presented in parts by weight per 100 parts by weight rubber unless otherwise stated. The following Tables also provide the results of some analytical testing that was performed on the compositions and/or vulcanizates prepared therefrom.

FORMATION OF EUTECTIC SOLVENT

[0092] A eutectic composition of choline chloride and urea was prepared by mixing one mole of choline chloride with two moles of urea at 100 °C to form a eutectic solvent, which was believed to be a deep eutectic solvent, which may be referred to as DES. The DES was allowed to cool to room temperature under standard conditions.

FORMATION OF VULCANIZABLE COMPOSITION

[0093] Vulcanizable compositions were prepared using the rubber formulation and mixing order provided in Table I. This rubber formulation was indicative of a rubber formulation that is useful in the manufacture of tire treads. As shown in Table I, the mix procedure was a three-step mix procedure including a masterbatch mix step, a “remill mix step,” and a final mix step. The various mixing steps were performed within a Banbury mixer. During preparation of the masterbatch, the mixer was operated at 75 rpm and a peak compositional temperature of 160 °C was attained. At that point in time, the composition was dropped from the mixer and allowed to cool to below about 85 °C. At this point in time, the composition was then reintroduced to the mixer along with the ingredients identified for the “remill stage,” and mixing was continued at 75 rpm and a peak compositional temperature of about 160 °C was achieved. The composition was again dropped from the mixer and allowed to cool to below about 50 °C. Then, the composition was again reintroduced to the mixer along with the ingredients identified for the “final mix stage.” Included among these ingredients was the DES, a DES blend, or a

carrier, as provided in Table II. As should be evident from Table II, in certain samples the DES and the inert carrier were introduced separately. These samples are labeled as comparative. In other samples, a preblend was made according to the invention wherein the DES and the inert carrier were combined prior to introducing the blend to the vulcanizable composition. These samples are labeled as inventive. The control sample simply included the DES without the addition of an inert carrier.

Table I

Ingredient	phr
Master	
SBR	70
BR	30
Carbon Black (N134)	25
Silica	50
Paraffinic oil	10
Wax	2
Stearic acid	2.78
6PPD (AO)	1
Remill	
Silica	10
Silane	6
Final	
Sulfur	2
Accelerators	4.09
ZnO	0.70
DES	0.25
Carrier	variable

[0094] Rheometer measurements were taken using an MDR 2000 operating at temperatures as specified in the Tables. The tensile mechanical properties (Max Stress, Modulus, Elongation, and Toughness) of the vulcanizates were measured by using the standard procedure described in ASTM-D412. The dynamic rheological properties (e.g. $\tan \delta$) of the vulcanizates were obtained from temperature-sweep studies, which were conducted over the range from about $-80\text{ }^{\circ}\text{C}$ to about $80\text{ }^{\circ}\text{C}$ and 10 Hz.

Table II

Samples:	Control	I-1	I-2	I-3	I-4	C-5	C-6	C-7
Variable								
DES (on carrier)	-	0.25	0.25	0.25	0.25	-	-	-
CaCO ₃	-	1.0	-	-	-	-	-	-
CaSiO ₃	-	-	1.0	0.5	-	-	-	-
SiO ₂	-	-	-	-	0.125	-	-	-
DES	0.25	-	-	-	-	0.25	0.25	0.25
CaCO ₃	-	-	-	-	-	1.0	-	-
CaSiO ₃	-	-	-	-	-	-	1.0	-
SiO ₂	-	-	-	-	-	-	-	0.5
MDR @ 171 °C								
MH-ML (dNm)	26.4	26.6	26.6	25.8	27.5	26.7	27.0	26.8
T2S (min)	1.08	0.90	0.87	1.03	0.93	0.87	0.95	0.96
T50 (min)	2.06	2.06	2.09	2.08	2.08	2.04	2.07	2.05
T90 (min)	4.04	3.85	4.17	4.17	4.33	4.18	4.21	4.19
Rheological Data								
Tanδ @ 0 °C	0.224	0.225	0.223	0.227	0.229	0.229	0.233	0.230
G' @ 30 °C (MPa)	19.6	19.8	20.3	19.1	19.0	19.3	19.9	20.4
Tanδ @ 60 °C	0.193	0.187	0.188	0.190	0.188	0.188	0.188	0.187
Tensile (23 °C)								
Max Stress (MPa)	14.6	14.5	14.6	13.6	11.8	15.5	12.9	13.8
M50 (MPa)	3.70	3.73	3.65	3.66	3.66	3.52	3.78	3.75
M100 (MPa)	7.11	7.13	7.00	7.09	7.07	6.73	7.26	7.21
M200 (MPa)	15.4	15.3	15.1	15.3	15.0	15.0	-	-
Strain @ Break (%)	191	195	196	179	158	209	167	180
Tensile (100 °C)								
Max Stress (MPa)	8.70	8.40	10.3	9.30	9.20	10.2	9.00	9.80
M50 (MPa)	3.40	3.42	3.40	3.41	3.37	3.32	3.43	3.47
M100 (MPa)	6.53	6.56	6.53	6.55	6.40	6.42	6.49	6.66
Strain @ Break (%)	129	126	152	138	138	151	135	141

[0095] The data in Table II shows that the presence of the inert carrier did not have an appreciable impact on cure properties, rheological properties, or tensile properties.

[0096] Various modifications and alterations that do not depart from the scope and spirit of this invention will become apparent to those skilled in the art. This invention is not to be duly limited to the illustrative embodiments set forth herein.

CLAIMS

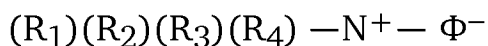
What is claimed is:

1. A process for preparing a rubber vulcanizate, the process comprising:
 - (i) providing a vulcanizable composition of matter including a sulfur-based curative and a eutectic composition blend, where the eutectic composition blend includes a eutectic composition and an inert carrier; and
 - (ii) heating the vulcanizable composition to thereby effect vulcanization.
2. The process of claim 1, where the vulcanizable composition includes a metal compound, and where said metal compound is zinc oxide.
3. The process of any of the preceding claims, where said vulcanizable composition is formed by providing a vulcanizable rubber and introducing a sulfur-based curative and a eutectic composition blend to the vulcanizable composition.
4. The process of any of the preceding claims, where said zinc oxide and said eutectic composition blend are introduced separately and individually to the vulcanizable rubber.
5. The process of any of the preceding claims, where said zinc oxide and said eutectic composition blend are pre-combined prior to being introduced to the vulcanizable composition.
6. The process of any of the preceding claims, where said vulcanizable composition includes less than 2 pbw zinc oxide per 100 pbw rubber.
7. The process of any of the preceding claims, where the eutectic composition is formed by combining choline chloride and urea.

8. The process of any of the preceding claims, where the vulcanizable composition includes from about 0.005 to about 3 pbw of the eutectic composition per 100 pbw rubber.
9. The process of any of the preceding claims, where the vulcanizable composition further includes a reinforcing filler, a resin, and an oil.
10. The process of any of the preceding claims, wherein the resin is selected from the group consisting of phenolic resins and hydrocarbon resins, and combinations thereof.
11. The process of any of the preceding claims, wherein the resin is selected from the group consisting of cycloaliphatic resins, aliphatic resins, aromatic resins, terpene resins, and combinations thereof.
12. The process of any of the preceding claims, wherein the resin is present in an amount of greater than 15 parts by weight resin per 100 parts by weight rubber.
13. The process of any of the preceding claims, wherein the resin is present in an amount of greater than 25 parts by weight resin per 100 parts by weight rubber.
14. The process of any of the preceding claims, wherein the resin is present in an amount of greater than 35 parts by weight resin per 100 parts by weight rubber.
15. The process of any of the preceding claims, wherein the reinforcing filler is silica.
16. The process of any of the preceding claims, wherein the silica is present in an amount of at least 25 parts by weight silica per 100 parts by weight rubber.

17. The process of any of the preceding claims, wherein the silica is present in an amount of at least 50 parts by weight silica per 100 parts by weight rubber.
18. The process of any of the preceding claims, wherein the silica is present in an amount of at least 70 parts by weight silica per 100 parts by weight rubber.
19. The process of any of the preceding claims, wherein the oil is selected from the group consisting of aromatic oils, paraffinic oils, naphthenic oils, vegetable oils other than castor oils, and low PCA oils including heavy naphthenic oils.
20. The process of any of the preceding claims, wherein the oil is a plant-sourced oil.
21. The process of any of the preceding claims, where eutectic composition is defined by the formula Cat^+X^-zY , where Cat^+ is a cation, X^- is a counter anion (e.g. Lewis Base), and z refers to the number of Y molecules that interact with the counter anion (e.g. Lewis or Bronsted Acid).
22. The process of any of the preceding claims, where Cat^+ is an ammonium, phosphonium, or sulfonium cation and X^- is a halide ion.
23. The process of any of the preceding claims, where the eutectic composition is selected from the group consisting of Type I, Type II, Type III, and Type IV eutectic compositions.
24. The process of any of the preceding claims, where the eutectic composition is formed by combining an ammonium compound with a metal halide, a metal halide hydrate, or a hydrogen bond donor.

25. The process of any of the preceding claims, where the ammonium compound may be defined by the formula II:



where each R_1 , R_2 , R_3 , and R_4 is individually hydrogen or a monovalent organic group, or, in the alternative, two of R_1 , R_2 , R_3 , and R_4 join to form a divalent organic group, and Φ^- is a counter anion.

26. The process of any of the preceding claims, where the ammonium compound is selected from the group consisting of N-ethyl-2-hydroxy-N,N-dimethylethanaminium chloride, 2-hydroxy -N,N,N-trimethylethanaminium chloride (which is also known as choline chloride), and N-benzyl-2-hydroxy-N,N-dimethylethanaminium chloride
27. The process of any of the preceding claims, where the ammonium compound is selected from the group consisting of and 2-chloro-N,N,N-trimethylethanaminium (which is also referred to as chlorcholine chloride), and 2-(chlorocarbonyloxy)-N,N,N-trimethylethanaminium chloride.
28. The process of any of the preceding claims, where the hydrogen bond donor is selected from the group consisting of amines, amides, carboxylic acids, and alcohols.
29. The process of any of the preceding claims, where the hydrogen bond donor is selected from the group consisting of aliphatic amines, ethylenediamine, diethylenetriamine, aminoethylpiperazine, triethylenetetramine, tris(2-aminoethyl)amine, N,N'-bis-(2-aminoethyle)piperazine, piperazinoethylethylenediamine, and tetraethylenepentaamine, propyleneamine, aniline, substituted aniline, and combinations thereof.

30. The process of any of the preceding claims, where the hydrogen bond donor is selected from the group consisting of urea, 1-methyl urea, 1,1-dimethyl urea, 1,3-dimethylurea, thiourea, urea, benzamide, acetamide, and combinations thereof.
31. The process of any of the preceding claims, where the hydrogen bond donor is selected from the group consisting of phenylpropionic acid, phenylacetic acid, benzoic acid, oxalic acid, malonic acid, adipic acid, succinic acid, citric acid, tricarballic acid, and combinations thereof.
32. The process of any of the preceding claims, where the hydrogen bond donor is selected from the group consisting of aliphatic alcohols, phenol, substituted phenol, ethylene glycol, propylene glycol, resorcinol, substituted resorcinol, glycerol, benzene triol, and mixtures thereof.
33. The process of any of the preceding claims, where the metal halide is selected from the group consisting of aluminum chloride, aluminum bromide, aluminum iodide, zinc chloride, zinc bromide, zinc iodide, tin chloride, tin bromide, tin iodide, iron chloride, iron bromide, iron iodide, and combinations thereof.
34. The process of any of the preceding claims, where eutectic composition is provided with a carrier.
35. The process of any of the preceding claims, where the carrier is a solid.
36. The process of any of the preceding claims, where the carrier is zinc oxide.
37. The process of any of the preceding claims, where the carrier is a eutectic member.

38. The process of any of the preceding claims, where the eutectic composition is a eutectic solvent at standard conditions.
39. The process of any of the preceding claims, where the eutectic composition is a deep eutectic solvent.
40. The process of any of the preceding claims, where the inert carrier is selected from the group consisting of calcium carbonate, wollastonite, silicon dioxide, and mixture of two or more thereof.
41. The process of any of the preceding claims, where the median diameter of the inert carrier is less than 200 nm.
42. The process of any of the preceding claims, where the weight ratio of eutectic composition to carrier is from about 0.05:1 to about 5:1.
43. A vulcanizate prepared from the process of any of the preceding claims.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2022/012112

A. CLASSIFICATION OF SUBJECT MATTER		
C08C 19/20(2006.01)i; C08K 3/22(2006.01)i; C08K 3/36(2006.01)i; C08K 3/16(2006.01)i; C08K 5/17(2006.01)i; C08K 5/09(2006.01)i; C08K 5/053(2006.01)i; C08L 21/00(2006.01)i; C08L 101/00(2006.01)i		
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) C08C 19/20(2006.01); C08C 19/42(2006.01); C08J 3/24(2006.01); C08J 5/18(2006.01); C08L 11/00(2006.01); F16F 9/04(2006.01)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean utility models and applications for utility models Japanese utility models and applications for utility models		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKOMPASS(KIPO internal) & Keywords: rubber vulcanizate, curative, eutectic, inert carrier, silica, calcium carbonate		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2019-089788 A1 (BRIDGESTONE CORPORATION) 09 May 2019 (2019-05-09) See claims 1-3, 11, 17, 36.	1-3
Y	ÜNLÜ, AYSE EZGI et al., 'Use of deep eutectic solvents as catalyst: A mini-review', Green Processing and Synthesis, 2019.05.18, vol. 8, no. 1, pp. 355-372 See pages 355, 359.	1-3
A	WO 2020-223028 A1 (FIRESTONE BUILDING PRODUCTS COMPANY, LLC) 05 November 2020 (2020-11-05) See the whole document.	1-3
A	US 2014-0217656 A1 (AGARWAL, SHEEL P.) 07 August 2014 (2014-08-07) See the whole document.	1-3
A	MAKOŠ, PATRYCJA et al., 'Silica gel impregnated by deep eutectic solvents for adsorptive removal of BTEX from gas streams', Materials, 2020.04.17, vol. 13, no. 8, article no. 1894(internal pages 1-17) See the whole document.	1-3
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "D" document cited by the applicant in the international application "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 28 April 2022		Date of mailing of the international search report 29 April 2022
Name and mailing address of the ISA/KR Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon 35208, Republic of Korea Facsimile No. +82-42-481-8578		Authorized officer HEO, Joo Hyung Telephone No. +82-42-481-5373

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.: **4-43**
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/US2022/012112

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
WO	2019-089788	A1	09 May 2019	CN	111315786	A	19 June 2020
				EP	3704162	A1	09 September 2020
				EP	3704162	A4	11 August 2021
				JP	2021-501244	A	14 January 2021
				US	2021-0198459	A1	01 July 2021

WO	2020-223028	A1	05 November 2020	None			

US	2014-0217656	A1	07 August 2014	DE	112012002208	B4	29 April 2021
				DE	112012002208	T5	03 July 2014
				US	9163689	B2	20 October 2015
				WO	2012-162462	A1	29 November 2012
