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(54) **Title:** PNEUMATIC TIRE AND ELASTOMERIC ARTICLES HAVING AROMA-EMITTING FUNCTIONALITY

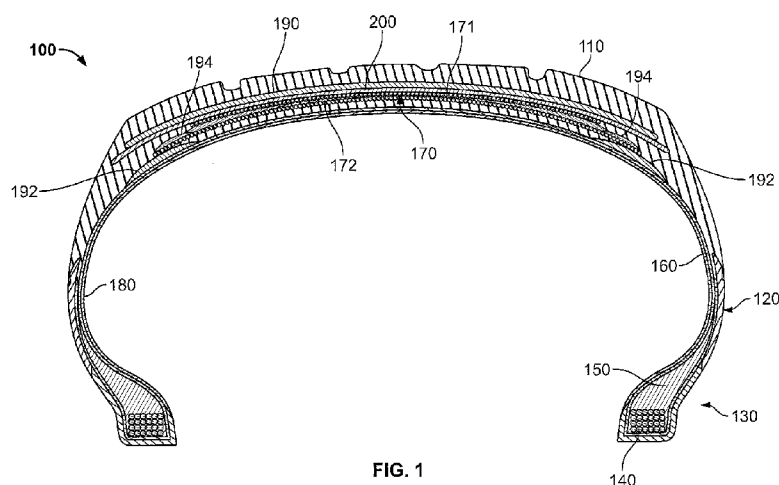


FIG. 1

(57) **Abstract:** A pneumatic tire is disclosed having an indicator of tire wear condition. The pneumatic tire has a circumferential tread and a pair of sidewalls, at least one of which comprises a barrier layer and an indicator layer, where the barrier layer is located above or outward from the indicator layer, which comprises a tire rubber composition having at least one fragrant chemical. A pneumatic tire is also disclosed having an indicator of elevated tire temperature. At least one of the tire portions comprises a tire rubber composition having thermally-activated fragrant chemical. Further, a pneumatic tire is disclosed comprising a tire rubber composition having polymeric or resinous microcapsules containing at least one fragrant chemical.



PNEUMATIC TIRE AND ELASTOMERIC ARTICLES HAVING AROMA-EMITTING FUNCTIONALITY

FIELD

[0001] One or more embodiments of the present disclosure relate to pneumatic tires comprised of rubber and exhibiting an odor that is not normally associated with articles made from rubber.

SUMMARY

[0002] A pneumatic tire is disclosed having an indicator of tire wear condition. The pneumatic tire has a circumferential tread and a pair of sidewalls. At least one of the tread and sidewalls comprises a barrier layer and an indicator layer, where the barrier layer is located above or outward from the indicator layer. The indicator layer comprises a tire rubber composition having between 0.1 and 100 phr of at least one fragrant chemical.

[0003] A pneumatic tire is disclosed having an indicator of elevated tire temperature. The pneumatic tire has a circumferential tread portion, a pair of sidewall portions, a pair of steel belt plies layered one on top of the other, a rubber belt edge insert between the edges of the layered steel belt plies and a rubber wedge between the inner steel belt ply edge and the body ply. At least one of these tire portions comprises a tire rubber composition having from 0.1 to 20 phr of a thermally-activated fragrant chemical.

[0004] A pneumatic tire is disclosed comprising a circumferential tread portion, a pair of sidewall portions, a pair of bead region portions, at least one cap, carcass ply, or belt ply, and an inner liner portion, where at least one of the tread and sidewalls may comprise a barrier layer and an indicator layer, where the barrier layer is located above or outward from the indicator layer. At least one of these tire portions comprises a tire rubber composition having from 0.1 to 100 phr of polymeric or resinous microcapsules containing at least one fragrant chemical. Encapsulating fragrant chemicals whose boiling points are lower than mixing and tire curing temperatures can nonetheless be used in a tire since the chemicals are contained within a capsule during mixing and curing. The fragrant chemicals can be

released at a slower rate from the tire than without encapsulation, since their release rate is limited by their diffusion rate not only through the tire rubber, but also through the capsule. Retention of the fragrance by the microcapsule wall until the wall is mechanically ruptured can serve as an indicator of abrasion of the tread indicator layer or abrasion of a sidewall indicator layer due to sidewall scuffing. A capsule is a core of one or more fragrant chemicals with or without a diluent surrounded or enveloped by a wall of yet another substance. Microcapsules can range in size from about 0.01 μm to 200 μm . In tire applications, a preferred size is less than about 10 μm .

[0005] The present disclosure also discloses a pneumatic tire comprising a circumferential tread and an interior portion located below the circumferential tread. The interior portion comprises a pair of sidewall portions, a pair of bead region portions, at least one cap, carcass ply, or belt ply, and an inner liner portion. At least one interior portion component comprises a tire rubber composition having from 0.1 to 60 phr of at least one fragrant chemical.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] In the accompanying drawing, structure is illustrated that, together with the detailed description provided below, describes exemplary embodiments of a tire exhibiting an odor that is not normally associated with pneumatic tires. One of ordinary skill in the art will appreciate that a single component may be designed as multiple components or that multiple components may be designed as a single component.

[0007] Further, in the accompanying drawing and description that follows, the figures are not drawn to scale and the proportions of certain parts have been exaggerated for convenience of illustration.

[0008] Figure 1 illustrates a cross-sectional view of one embodiment of a pneumatic tire provided according to this disclosure.

DETAILED DESCRIPTION

[0009] The following includes definitions of selected terms employed herein. The definitions include various examples and/or forms of components that fall

within the scope of a term and that may be used for implementation. The examples are not intended to be limiting. Both singular and plural forms of terms may be within the definitions.

[0010] “Axial” or “axially” refer to a direction that is parallel to the axis of rotation of a tire;

[0011] “Cord” refers to polymeric or metallic material in a strand or cable, used to form the belts, plies and/or beads of a tire;

[0012] “Circumferential” and “circumferentially” refer to lines or directions extending along the perimeter of the surface of the tread parallel to the equatorial plane perpendicular to the axial direction of the tire;

[0013] “Equatorial plane” refers to the plane that is perpendicular to the tire’s axis of rotation and passes through the center of the tire’s tread;

[0014] “Layer” refers to a portion of a pneumatic tire that comprises a distinct elastomeric formulation, as compared to surrounding layers, or a portion that has been formed or processed into the tire separately from other layers, or both;

[0015] “Monomer” refers to any compound with a polymerizable moiety which is added to a reactor in order to produce a polymer;

[0016] “Phr” refers to parts by weight of an ingredient per 100 parts by weight of rubber;

[0017] “Polymer” refers to a macromolecular compound prepared by polymerizing monomers of the same or a different type, and generally denotes homopolymers, copolymers, interpolymers, and the like; the term “interpolymer” refers to polymers prepared by the polymerization of at least two types of monomers;

[0018] “Radial” or “radially” refer to a direction perpendicular to the axis of rotation of the tire;

[0019] “Sidewall” refers to that portion of the tire between the tread and the bead;

[0020] “Tire component” refers to a portion of a tire that has been formed and incorporated into the green tire assembly in a separate process step than any other tire component; examples of separate tire components include the sidewalls, bead portion, cap ply, belt ply, carcass ply and inner liner portions, tire tread, sub-tread and a combination of the tire tread and sub-tread; and,

[0021] “Tread” refers to the tire component that comes into contact with the road under normal load.

[0022] Directions are also stated in this disclosure with reference to the axis of rotation of the tire. The terms “upward” and “upwardly” refer to a general direction towards the tread of the tire, whereas “downward” and “downwardly” refer to the general direction towards the axis of rotation of the tire. Thus, when relative directional terms such as “upper” and “lower” are used in connection with an element, the “upper” element is spaced closer to the tread than the “lower” element. Additionally, when relative directional terms such as “above” or “below” are used in connection with an element, an element that is “above” another element is closer to the tread than the other element.

The terms “inward” and “inwardly” refer to a general direction towards the equatorial plane of the tire, whereas “outward” and “outwardly” refer to a general direction away from the equatorial plane of the tire and towards the sidewall of the tire. Thus, when relative directional terms such as “inner” and “outer” are used in connection with an element, the “inner” element is spaced closer to the equatorial plane of the tire than the “outer” element.

[0023] Throughout this document, all values given in the form of percentages are weight percentages unless the surrounding text explicitly indicates a contrary intention. The relevant portions of any patent or patent publication mentioned are incorporated herein by reference.

Pneumatic Tires

[0024] A pneumatic tire construct is generally known in the art, and the present disclosure is intended to be inclusive of any tire construct that incorporates the limitations and functions in the manner described herein.

[0025] Figure 1 depicts a cross-sectional view of an exemplary pneumatic tire 100 according to the present disclosure. Tire 100 includes a circumferential tread 110, a pair of sidewalls 120 which terminate in a pair of axially spaced bead regions that are indicated generally at 130. Further, tire 100 includes carcass ply 160, which extends circumferentially about the tire and axially from one bead region to the other, through sidewalls 120 and beneath the tread of the tire. Carcass ply 160 generally comprises parallel-aligned cords (not shown) that may be biased or aligned with the equatorial plane. Bead regions 130 generally include an annular ring (*e.g.*, a bundle of steel cables) 140, about which carcass ply 160 is generally turned-up. The area between carcass ply 160 that is turned-up is generally filled with bead filler 150.

[0026] With continued reference to Figure 1, tire 100 further includes belt 170, comprising a first layer 171 and second layer 172, that extends circumferentially about the tire between tread 110 and carcass ply 160. Belt 170 may optionally be a belt ply comprising parallel-aligned cords (not shown) that are biased with the equatorial plane. Belt edge inserts 192 are placed between the carcass ply 160 and belt 170, while belt wedge inserts 194 are placed between individual belt layers 171, 172 comprising belt 170. Tire 100 also includes inner liner 180, that is generally a layer lining the inside portion of a tire that has a high resistance to air permeability to ensure air retention when the tire is inflated. Tire 100 may also include sub-tread layer 190, provided between tread 110 and belt 170. Tire 100 may also include cap ply 200, provided between sub-tread layer 190 and belt 170, where the cords of the cap ply 200 may be aligned with the equatorial plane. Typically, one or more of the carcass, cap, and belt plies are coated with a rubber composition, known generally as a “skim stock” rubber. The carcass ply cord material may be coated with a relatively thick rubber layer, and is therefore also sometimes referred to as “carcass ply rubber.”

[0027] It is readily understood that various other components, such as gum abrasions strips, hard rubber bead reinforcement strips adjacent the bead area, as well as other reinforcement strips regularly used in the shoulder, sidewalls and bead areas of the tire may be used in forming a pneumatic tire. It is also understood that

additional layers, including but not limited to additional cap, ply, and belt layers, may be used in forming a pneumatic tire.

Tire Rubber Compositions

[0028] A number of tire components are comprised of a tire rubber composition, including but not limited to tread rubber compositions, sidewall rubber compositions, inner liner rubber compositions, bead filler compositions, skim rubber compositions, and the like. Tire rubber compositions are comprised of at least one elastomer, including but not limited to natural or synthetic rubber, or blends thereof. The use of the term “elastomer” and “rubber” are used interchangeably herein. Generally any conventionally-used elastomer for rubber compounding is suitable for use herein. Non-limiting examples include the following, individually as well as in combination, according the desired final viscoelastic properties of the rubber compound: Natural Rubber (Hevea and Guayule), Polyisoprene Rubber, Styrene Butadiene Rubber, Polybutadiene Rubber, Butyl Rubbers, Halobutyl Rubbers, Ethylene Propylene Rubbers, Crosslinked Polyethylene, Neoprenes, Nitrile Rubbers, Chlorinated Polyethylene Rubbers, Silicone Rubbers, Specialty Heat & Oil Resistant Rubbers, Other Specialty Rubbers, and Thermoplastic Rubbers, as such terms are employed in *The Vanderbilt Rubber Handbook*, Thirteenth Edition, (1990). The elastomers may contain a variety of functional groups, including but not limited to, tin, silicon, and amine-containing functional groups.

[0029] In addition to elastomeric content, a tire rubber composition typically also contains any or all of the following additional ingredients: fillers, processing oils/aids, antidegradants, zinc oxide, stearic acid, sulfur, accelerators, coupling agents, and adhesion promoters, and the like. When utilized, such additional ingredients may be present in the following exemplary amounts: (1) fillers: from 0 to 150 phr, and preferably from 20 to 80 phr; (2) processing oils/aids: from 0 to 75 phr, and preferably from 0 to 50 phr; (3) antidegradants: from 0 to 10 phr, and preferably from 0 to 5 phr; (4) stearic acid: from 0 to 5 phr, and preferably from 0 to 3 phr; (5) zinc oxide: from 0 to 10 phr, and preferably from 0 to 5 phr; (6) sulfur: from 0 to 10 phr, and preferably from 0 to 4 phr; (7) accelerators: from 0 to 10 phr,

and preferably from 0 to 5 phr; (8) coupling agent: from 0 to 30 phr, and preferably from 0.5 to 15 phr; and (9) adhesion promoters: preferably from 1 to 12 phr.

[0030] When forming tire rubber compositions, generally all ingredients may be mixed with standard equipment such as, *e.g.*, Banbury mixers or other internal mixers. Typically, mixing occurs in two or more stages, during which ingredients may be added. In the case of mixing a tire tread rubber composition, typically the mixing process is comprised of a masterbatch initial mixing stage, followed by additional non-productive mixing stage(s), and ending with a final, productive (curative containing) mixing stage.

[0031] During the masterbatch stage, mixing typically is begun at temperatures of about 90°C to about 130°C and increases until a so-called drop temperature, typically about 165°C, is reached. Typically, ingredients such as elastomers, fillers, oils and processing aids, antioxidants and antiozonants, zinc oxide and stearic acid, are added during the initial masterbatch. The initial masterbatch may be followed by a “re-mill”, in which additional fillers and additives are added, or a non-productive re-mill mixing stage in which no ingredients are added. The re-mill stage often is performed at temperatures similar to, although often slightly lower than, those employed in the masterbatch stage, *i.e.*, ramping from about 90°C to a drop temperature of about 150°C. One skilled in the art may select the most appropriate type of mixing. For purposes of this disclosure, the term “masterbatch” means the composition that is present during the initial masterbatch stage or the composition as it exists during any subsequent re-mill stage, or both.

[0032] A final mixing stage is then employed, during which curatives (*e.g.*, sulfur or peroxide-based curing systems), including accelerators, and additional processing aids and antioxidants/antiozonants may be added. The fragrant chemical may be added to the mixture at this stage, resulting in the aroma-emitting tire component according to the present disclosure. For a general disclosure of suitable curatives, see Kirk-Othmer, *Encyclopedia of Chem. Tech.*, 3d ed., (Wiley Interscience, New York, 1982), vol. 20, pp. 365-468. To avoid undesirable scorching, premature onset of vulcanization or vaporization of the fragrant chemical when not encapsulated, this mixing step often is done at lower temperatures, *e.g.*, starting at about 60°C to

about 65°C and not going higher than about 105°C to about 110°C. This final mixing stage may also be followed by a non-productive mixing stage in which no ingredients are added. One skilled in the art may select the most appropriate type of mixing to achieve a vulcanizable rubber compound according to the present disclosure. For purposes of this disclosure, the term “final batch” means the composition that is present during the final mixing stage, or any subsequent non-productive stage. It should be noted that fragrant chemicals may be introduced during a productive and non-productive mixing stages. An alternate to forming tire rubber compositions using internal mixers is the forming of rubber compositions using solution master batching (see for example U.S. Published Patent Application No. 20070155890). In solution master batching, the polymer of the rubber composition is dissolved or suspended in a solvent in a vat or vessel to which other typical compounding ingredients are added, and where the mixing of ingredients is typically accomplished with an agitator or pump or other dispersive device. The solution or suspension of polymer may be the polymer cement created during polymerization itself. The mixing temperature is generally about 22°C. After adequate dispersion of the ingredients, the solvent is removed from the mixture and the solid rubber composition is collected. The composition may contain all of the ingredients suitable for subsequent vulcanization of a finished rubber product, or the composition may require additional ingredients added subsequently in an internal mixer to provide a final vulcanizable rubber composition. Solution master batching allows for the combining of rubber ingredients at lower temperatures and with less shear stress than does internal mixing, where the lower shear of solution master batching, compared to internal mixing, would enhance the survivability of capsules containing fragrant chemicals, and vaporization of fragrant chemicals added neat would be minimized, due to the lower mixing temperature.

[0033] The means for building tires are usually semi-automated and well documented in the literature. Multiple types of different tire rubber compositions (*e.g.*, sidewall rubbers, innerliner rubbers, bead filler rubbers, carcass ply rubbers, skim stock rubbers and tread rubbers) are assembled along with rubber-coated metal beads and metal plies to form a conventional vehicle tire. The selection of

specific metal alloys and elastomeric compounds, and the configuration and dimensions of the various metallic and elastomeric components is also well understood by those skilled in the art of tire building.

[0034] Finally, a “green” tire is assembled, followed by curing in a press mold at a temperature about 5°C to about 15°C higher than the highest temperatures employed during the mixing stages, most commonly about 170°C, concurrently crosslinking the elastomeric components and molding the elastomeric components into a final tire.

Fragrant Chemicals

[0035] “Fragrant chemical” as used herein may be any fragrant chemical or perfume, or mixtures thereof, that emits an odor that is not normally associated with tire rubber compositions, or products made therefrom, suitable for use herein, including but not limited to fragrant chemical encapsulated by various materials using various techniques including microcapsule walls comprised of polymeric materials, or a fragrant chemical that melts or vaporizes at a selected elevated temperature, as described herein. Other non-limiting examples include fine fragrances, fabric perfumes, and deodorant perfumes and others comprising a wide range of ethers, esters, aldehydes, alcohols, lactones, linear terpenes, cyclic terpenes, amines, aromatics, ketones, thiols, acetals, organic acids, phenols and unsaturated cyclic and acyclic hydrocarbons. Non-limiting examples further include natural or synthetic fragrant oils, including argumen, allium, cedar, eucalyptus, andropogon, cymbopogon, lavandula, Mentha species, connifier family Pinacea, sage, juniper berry, dill, clove and other oils. In one or more embodiments, the fragrant oils are musks, rose oil, honeysuckle oil, pine oil, jasmine or oak moss, and combinations thereof. Fragrant chemicals suitable for use herein may generally be found in K. Bauer, “Common Fragrance and Flavor Materials --- Preparation, Properties and Uses” (VCH Publishers), Flavors & Fragrances Catalog (Sigma-Aldrich Fine Chemicals) (2004), S. Arctander, “Perfume Flavors and Chemicals” (1969), and S. Arctander, “Perfume and Flavor Materials of Natural Origin” (Allured Publ. Corp) (1994), the disclosures of which are incorporated herein by reference.

[0036] For the purpose of alerting the tire user to a potentially undesirable condition of the tire, such as a worn tread or a scuffed sidewall or a condition at the belt edge, the chosen fragrant chemicals may impart odors that are generally repulsive and otherwise undesirable. Organoleptic descriptions of these materials may include (see SAFC Specialties catalog "SAFC Flavors and Fragrances Domestic Edition" approximately 2005) strong, pungent, sour, repulsive, penetrating, garlic, fishy, pungent, sulfurous, disagreeable, rancid, sweat-like, sickening, acrid, metallic, unpleasant, ammonia, cabbage-like, cadaverous, fecal, intense, powerful, sharp and so on. Individual fragrant chemicals associated with some of the organoleptic properties immediately above include indole, skatole, 1,8-octanedithiol, 4-ethyl phenol, 2,6-dimethylthiophenol, acetic acid, trans-2-nonenal, acetal, and cuminaldehyde.

[0037] In one embodiment, one or more fragrant chemicals, the core, are encapsulated within another material, the shell or wall, different from the fragrant chemicals, in order to form a microcapsule. To one skilled in the art, there are multiple techniques for creating microcapsules including but not limited to coacervation, polymer-polymer phase separation, interfacial polymerization, dispersion polymerization, in situ polymerization, solvent phase separation, desolvation, precipitation, solvent evaporation, spray drying, spray chilling, matrix encapsulation and various types of fluid bed, extrusion and hybrid systems. To one skilled in the art, the microcapsule shell or wall may be a polymeric material, a sugar, a starch, fumed silica, proteins such as gelatin, or mixtures of polysaccharides and proteins such as gum arabic, among others. In some embodiments, a microcapsule wall that will allow a large fraction of the microcapsules to survive rubber mixing and the temperatures of mixing and curing is desirable. For polymeric microcapsules, the polymer comprising the microcapsule wall may be created during the encapsulation process itself, or an existing polymer may be added to the encapsulation mixture. Generally any suitable type and mode of manufacture of such polymeric microcapsule may be utilized herein. Typically, polymeric shells or walls encapsulating an active agent are produced through heterogeneous polymerization reactions, such as emulsion, dispersion, precipitation, interfacial and suspension

polymerizations, where polymerization may occur before or during the encapsulation process. The reaction mechanism is generally not limited, and includes addition polymerization, condensation polymerization and step polymerization. Polymers may be branched or crosslinked. Polymers formed through condensation or step polymerization may be branched or crosslinked by including a fraction of monomer that has more than two functional groups. Crosslinked, rigid polymers are sometimes referred to as resinous, and the prepolymers from which they may be formed are sometimes referred to as resins. Generally any monomer, oligomer, or polymer capable of addition, condensation or step polymerization may be suitable, with the proviso that it meets the functional requirements of the microcapsules described herein. Polymerization of thermosetting plastics may proceed starting from prepolymers, which are thermosetting materials whose polymerization is incomplete.

[0038] In another embodiment, the polymer of the microcapsule wall contains sulfur so that elastomer chains in the tire rubber compound can cross-link with polymer chains of the microcapsule polymeric wall. Polymer attachments to fillers are known in the industry to enhance rubber performance. As an example of a polymeric wall formed by condensation polymerization, a fraction of the diol monomers would have the general structure HO-R'-OH or a fraction of the diacid monomers would have the general structure HO₂C-R'-CO₂H, where R' has the general structure (CH₂)_x-S_y-(CH₂)_z, and where x and z can range from 1 to about 5 and y can range from 1 to about 6. Alternately, R' can be of the general structure

$$\begin{array}{c} \text{SH} \\ | \\ (\text{CH}_2)_x - \text{CH} - (\text{CH}_2)_y \end{array}$$

where x and y can range from 1 to about 5. The fraction of diol and diacid monomers that are replaced by sulfur containing monomer would range from about 0.01 to 1.0 and in another embodiment from about 0.01 to 0.50. Another example of a microcapsule wall that has the advantage of co-curing with the elastomer of the tire rubber component to which the microcapsules are added are aromatic and aliphatic polysulfides, where x of -S_x- in the polysulfide polymer chain backbone can range from 1 to about 6.

[0039] Monomer and reaction conditions may be varied to produce polymeric microcapsules having suitable properties for use herein, such as suitable glass transition temperature, hardness, solubility and polarity. In one or more embodiments, the microcapsule is a thermoplastic or thermoset material. Non-limiting examples of suitable polymers and polymer families include urea-formaldehyde polymers (urea and formaldehyde monomers), melamine-formaldehyde polymers (urea, melamine and formaldehyde monomers), phenol formaldehyde polymers (phenol and formaldehyde monomers), acrylic polymers (acrylic and methacrylic monomers), polyesters (diacid and diol monomers), polyamides (diamines, diols and amino acid monomers), polyimides (dianhydrides and diamine monomers), polysiloxanes (chlorosilane monomer), and poly (vinyl acetate) (vinyl acetate monomer). Additional polymers and polymer families are cellulose acetate, and aromatic and aliphatic polysulfides, where x of $-S_x-$ in the polysulfide polymer chain backbone can range from 1 to about 6. Microcapsule walls may include naturally occurring polymers such as alginate and cellulose.

[0040] In certain embodiments, the polymeric microcapsule is designed to allow a relatively slow effective release rate of the encapsulated fragrant chemical, depending on the desired duration of fragrant chemical release from the elastomeric article containing the microcapsules (*e.g.*, pneumatic tire). In one or more embodiments, the polymeric material is selected to allow effectively no release of the encapsulated fragrant material, and release fragrant chemical only when the microcapsule is shattered or broken. In other embodiments, the polymeric material is selected to provide a release rate resulting in a release of fragrant chemical from the elastomeric article in a relatively short time frame, such as a few months. The release rate is determined by such parameters as the diffusivity and solubility of the fragrant chemical in the polymeric material, the thickness and porosity of the polymeric material, the concentration of the fragrant chemical, and the polarity of the fragrant chemical and polymeric material.

[0041] In one or more embodiments, the polymeric microcapsules have a characteristic dimension between 0.1 and 1,000 microns. In other embodiments,

the polymeric microcapsules have a characteristic length between 0.1 and 100 microns; in yet other embodiments, between 0.1 and 10 microns.

[0042] In one non-limiting example, a polyurethane microcapsule encapsulating a fragrant cyclic or acyclic hydrocarbon is produced by mixing the hydrocarbon and an isocyanate monomer together with an emulsifier and mechanically dispersing the mixture into fine droplets (with finer droplets resulting in smaller microcapsules). An oligomeric amine in aqueous solution is added to the dispersion, forming microcapsules that encapsulate an amount of the fragrant hydrocarbon.

[0043] In another embodiment, the fragrant chemical, whether in the form of a microcapsule or a solid additive, is a solid at temperatures below the temperature where it is used to signal potential over heating of a tire component. The fragrant chemical's melting point is in the neighborhood of 70°C to 130°C. While this temperature range includes discharge temperatures of the final mixing stage (the fragrance would be added during or subsequent the final batch stage), and temperatures associated with tire curing, if the fragrant chemical is not soluble in the rubber component, it will re-crystallize upon cooling, when the tire is removed from the curing mold. Since the curing mold is under pressure, release of the fragrance through melting and liquid migration to the tire surface is mitigated. In final stage mixing, the rubber batch temperature is above 90°C for typically less than one minute, during which migration and release of the melted fragrance is not expected. Non-limiting examples of fragrances that have melting points above room temperature are phenoxyacetic acid (m.p. = 98°C – 101°C), skatole (92°C – 97°C), and benzoic acid (m.p. = 121°C – 124°C).

Indicator Of Tire Wear Condition

[0044] In one embodiment, a pneumatic tire is disclosed having an indicator of tire wear condition, comprising circumferential tread and a pair of sidewalls. At least one of the tread and sidewalls comprises a barrier layer and an indicator layer, and the barrier layer is located above or outwardly from the indicator layer. The indicator layer comprises a tire rubber composition having between 0.1 and 100 phr of at least one of the fragrant chemicals described above.

[0045] In general, the relationship of the barrier layer and indicator layer is as follows: the barrier layer is located above (*i.e.*, more proximate the tread of the tire) or outward (*i.e.*, further the equatorial plane of the tire and more proximate the sidewall) relative to the indicator layer, and aids in preventing fragrant chemical from escaping the indicator layer or in preventing microcapsules in the indicator layer from breaking and releasing fragrant chemical, until such time as the barrier layer is worn away or breached, thereby exposing the indicator layer to the atmosphere and road surface. It should be understood that the use of multiple barrier layers and/or multiple indicator layers is contemplated herein.

[0046] The indicator layer is designed to carry a sufficient level of fragrant chemicals so that exposure of a portion of the indicator layer to the atmosphere will result in an odor that is strong enough to alert a person that the barrier layer has been worn away or breached. This is determined both by the thickness of the barrier layer and the propensity of the indicator layer composition material to retain fragrant chemicals.

[0047] In one embodiment, the composition of the indicator layer is substantially similar to the composition of the barrier layer, with a material exception that the indicator layer includes an amount of polymeric or resinous microcapsules encapsulating an amount of fragrant chemical, described above. In another embodiment, the composition of the indicator layer is substantially different than the composition of the barrier layer, such that elastomeric content of the indicator layer is selected to retain an amount of fragrant chemical described above, and the elastomeric content of the barrier layer is selected such that the fragrant chemical has little or no diffusivity through the material.

[0048] In one or more embodiments, the indicator layer comprises a rubber composition suitable for the tire tread or tire sidewall, or both, in which all or a portion of the process oil plus other processing aids, are replaced or supplemented with at least one fragrant oil. Non-limiting examples include a tread rubber or sidewall rubber composition containing between 0.1 and 60 phr fragrant oil; in others, between 0.1 and 30 phr fragrant oil. In yet other embodiments, no fragrant

oils are added to the tread or sidewall, but instead are added to other tire components.

[0049] In one or more embodiments, the indicator layer comprises a tire tread rubber composition or tire sidewall rubber composition, or both, in which at least one fragrant chemical (e.g., polymeric or resinous microcapsules containing at least one fragrant chemical) is added above formula in an amount of 0.1 to 20 phr. In one or more embodiments, the indicator layer comprises a tire tread rubber composition or tire sidewall rubber composition, or both, in which all or a portion of the filler is replaced with polymeric or resinous microcapsules containing at least one fragrant chemical. Non-limiting examples include a tread rubber or sidewall rubber composition containing between 0.1 and 100 phr polymeric or resinous microcapsules; in others, between 0.1 and 60 phr polymeric or resinous microcapsules.

[0050] In one or more embodiments, the barrier and indicator layers are different tire components. In one non-limiting example, the barrier layer is the tire tread component and the indicator layer is the sub-tread component. In one embodiment, the tire tread contains no fragrant chemicals and the sub-tread contains between 0.1 and 100 phr of polymeric or resinous microcapsules encapsulating at least one fragrant chemical; in another embodiment, the sub-tread contains between 0.1 and 60 phr of polymeric or resinous microcapsules encapsulating at least one fragrant chemical.

[0051] In another embodiment, the barrier layer and the indicator layer form a multi-layered tire tread or multilayered tire sidewalls. Methods for forming a multilayered tire component are known in the art, and include but are not limited to co-extrusion and application of successive layers of a tire on a building drum. See for example F. J. Kovac in "Science and Technology of Rubber", F. R. Eirich, Ed., Academic Press, New York, 1978, pg. 602. Methods for co-extruding a tire component are described in, for example, US Patent Nos. 6,994,817; 4,539,169; 4,556,376; 5,292,472 and 4,657,718, the disclosures of which are incorporated herein. In one embodiment, the tire tread is multilayered and comprises an indicator layer and a barrier layer above or outward from the indicator layer, where

the indicator layer comprises between 0.1 and 100 phr polymeric or resinous microcapsules encapsulating at least one fragrant chemical, as described above. In another embodiment, the microcapsules are selected from the polymer families consisting essentially of urea-formaldehyde polymers, melamine-formaldehyde polymers, phenol formaldehyde polymers, acrylic polymers, polyesters, polyamides, polyimides, polysiloxanes, and poly (vinyl acetate) microcapsules, and combinations thereof. Additional polymers and polymer families are cellulose acetate and aromatic and aliphatic polysulfides, where x of $-S_x-$ in the polymer chain backbone can range from 1 to about 6, microcapsules, and combinations thereof. In another embodiment, the tire tread is multilayered and has a total thickness of between 0.3 and 1.2 inches, where the upper portion is a barrier layer between 0.15 and 0.95 inches thick, and the lower portion is an indicator layer between 0.02 and 0.3 inches thick.

[0052] In yet another embodiment, the indicator layer comprises multiple constituent layers, where each constituent layers has a higher loading of fragrant chemicals than the constituent layer above or outward from it.

Indicator Of Elevated Tire Component Temperature

[0053] Elevated tire temperature may be an indicator of a deficient running condition, such as low tire pressure or high deformation at the belt edges. In general, due to excessive shear forces, low tire pressure may cause the temperature of the tire tread or sidewalls or belt edges, or all three, to exceed about 60 to 80°C.

[0054] In one or more embodiments described in this disclosure, an elevated temperature in any of the tread, sidewall, or belt edges of a tire may be indicated by incorporating a thermally-activated fragrant chemical, described above, in one or more of those regions, or in tire components adjacent one or more of those regions. The thermally-activated fragrant chemical is selected so that its effective release rate of fragrant chemical is sufficiently elevated at a threshold temperature (indicative of a deficient running condition), so that a person may detect an odor caused by the released fragrant chemical.

[0055] In one embodiment, at least one of the tread, sidewall, or belt edge regions of a tire comprise a tire rubber composition having from 0.1 to 20 phr of at least one thermally-activated fragrant chemical having a melting point between 80°C and 100°C; in other embodiments, between 100°C and 130°C.

[0056] In another embodiment, the belt edge insert, or the belt wedge or both contain between 0.1 to 20 phr of at least one thermally activated fragrant chemical having a melting point between 80°C and 100°C; in other embodiments, between 100°C and 130°C.

[0057] In another embodiment, the fragrant chemical or chemicals comprise the core of a microcapsule whose shell is a polymer with a glass transition temperature (T_g) greater than about 80°C and less than about 150°C. The effective diffusion rate of the core fragrant chemical through the microcapsule wall is sufficiently elevated at a threshold temperature (indicative of a deficient running condition) greater than T_g, so that a person may detect an odor caused by the released fragrant chemical.

Fragrant Tire

[0058] In addition to a tire that may release fragrant chemicals in response to tire wear or abnormal operating conditions, the present disclosure contemplates a tire that may release fragrant chemicals over time and without the need of tire wear or at abnormal operating conditions. This is accomplished generally by providing one or more tire components that have an amount of fragrant chemicals and that are designed to release the fragrant chemical at a desired effective release rate over time, as described above.

[0059] In one or more embodiments described in this disclosure, a pneumatic tire is provided where at least one of the circumferential tread portion, sidewall portions, bead region portions, cap, carcass, belt plies, belt edge insert or belt wedge and inner liner portions comprise a tire rubber composition having from 0.1 to 100 phr of polymeric or resinous microcapsules containing at least one fragrant chemical, described above; in another embodiment from 0.1 to 60 phr of such microcapsules.

[0060] In one embodiment, the tread portion comprises a tread rubber composition having from 0.1 to 100 phr of microcapsules containing at least one fragrant chemical, where the polymer of the microcapsule wall is an aromatic or aliphatic polysulfide containing between 1 and 6 moles of sulfur per monomer unit. In another embodiment, the tread rubber composition has from 0.1 to 60 phr of microcapsules, where the polymer of the microcapsule wall is an aromatic or aliphatic polysulfide containing between 1 and 6 moles of sulfur per monomer unit.

[0061] In one embodiment, the tread portion comprises a tread rubber composition having from 0.1 to 100 phr of microcapsules containing at least one fragrant chemical, where the polymer of the microcapsule wall is formed through condensation polymerization of diol monomers or diacid monomers, and where from about 1% to 100% or in another embodiment 1% to 50% of the diol or diacid monomers have the general structure HO-R'-OH or HO₂C-R'-CO₂H, respectively, and

where R' is $(\text{CH}_2)_x-\overset{\text{SH}}{\underset{|}{\text{CH}}}-(\text{CH}_2)_y$, and where x and y can range from 1 to about 5. In another embodiment, the tread rubber composition has from 0.1 to 60 phr of microcapsules, where the polymer of the microcapsule wall is formed through condensation polymerization of diol monomers or diacid monomers, and where from about 1% to 100% and in another embodiment from 1% to 50% of the diol or diacid monomers have the general structure HO-R'-OH or HO₂C-R'-CO₂H,

respectively, and where R' is $(\text{CH}_2)_x-\overset{\text{SH}}{\underset{|}{\text{CH}}}-(\text{CH}_2)_y$, and where x and y can range from 1 to about 5.

[0062] In one embodiment, the tread portion comprises a tread rubber composition having from 0.1 to 100 phr of polymeric microcapsules containing at least one fragrant chemical; in another, from 0.1 to 60 phr of polymeric microcapsules containing at least one fragrant chemical. In yet another embodiment, the microcapsules are selected from the group consisting essentially of urea-formaldehyde, melamine-formaldehyde, phenol formaldehyde, acrylic, polyester, polyamide, polyimide, polysiloxane, poly (vinyl acetate), cellulose acetate

and aromatic aliphatic polysulfides, where x of $-S_x-$ in the polysulfide polymer chain backbone can range from 1 to about 6, microcapsules, and combinations thereof.

[0063] In one or more embodiments described in this disclosure, a pneumatic tire is provided comprising a circumferential tread and an interior portion located below the tread that comprises a pair of sidewall portions, a pair of bead region portions, at least one cap, carcass, or belt ply, belt edge inserts, belt wedge, and an inner liner portion and where at least one interior portion component comprises a tire rubber composition having from 0.1 to 60 phr of at least one fragrant chemical, described above. In one embodiment, the fragrant chemical is a fragrant oil. In another embodiment, the fragrant oil is selected from the group consisting essentially of argumen, allium, cedar, eucalyptus, andrpogon, cymbopogon, lavandula, Mentha species, connifier family Pinacea, sage oils, and combinations thereof.

[0064] In certain embodiments, one or more of the cap, carcass, and belt plies comprise polymeric fiber that retains an amount of at least one fragrant chemical. In general, cap, carcass, and belt plies may be made of interwoven or aligned polymeric cord or additionally steel cord in the case of belt plies. Non-limiting examples of suitable cord material are nylons, polyesters, aramids, cotton, polynorbornene and rayons.

[0065] In one or more embodiments, at least one of the cap, carcass, and belt plies is selected from the group consisting essentially of nylon, polyester, aramid, cotton, polynorbornene and rayon fibers and retains from 0.1% to 10% by weight of at least one fragrant chemical; in others, the at least one ply retains from 0.1% to 5% by weight of at least one fragrant chemical. The manner of incorporating the fragrant chemical in the ply fiber is not material to the present disclosure; a non-limiting example is to immerse the fiber in a solution of the fragrant chemical, or in the chemical itself.

[0066] To the extent that the term “includes” or “including” is used in the specification or the claims, it is intended to be inclusive in a manner similar to the term “comprising” as that term is interpreted when employed as a transitional word in a claim. Furthermore, to the extent that the term “or” is employed (e.g., A or B) it

is intended to mean “A or B or both.” When the applicants intend to indicate “only A or B but not both” then the term “only A or B but not both” will be employed. Thus, use of the term “or” herein is the inclusive, and not the exclusive use. See, Bryan A. Garner, *A Dictionary of Modern Legal Usage* 624 (2d. Ed. 1995). Also, to the extent that the terms “in” or “into” are used in the specification or the claims, it is intended to additionally mean “on” or “onto.” Furthermore, to the extent the term “connect” is used in the specification or claims, it is intended to mean not only “directly connected to,” but also “indirectly connected to” such as connected through another component or components.

[0067] While the present disclosure has been illustrated by the description of embodiments thereof, and while the embodiments have been described in considerable detail, it is not the intention of the applicants to restrict or in any way limit the scope of the appended claims to such detail. Additional advantages and modifications will readily appear to those skilled in the art. Therefore, the disclosure, in its broader aspects, is not limited to the specific details, the representative apparatus, and illustrative examples shown and described. Accordingly, departures may be made from such details without departing from the spirit or scope of the applicant’s general inventive concept.

Exemplary Formulation

[0068] A prophetic example of a formulation according to the present disclosure are as follows. Various ingredients were added during the master batch stage for both the tread and for an indicator layer, as shown in Table 1.

Table 1		
Ingredient	Tread (phr)	Indicator Layer (phr)
Solution SBR	100.0	100.0
N351 carbon black	55.0	55.0
stearic acid	2.0	2.0
naphthenic oil	10.0	10.0

ZnO	3.0	3.0
Antioxidant	1.0	1.0
wax	2.0	2.0
Total:	173.0	173.0

[0069] The master batch may be mixed according to the following procedure. The mixer is preheated to 90°C to 100°C and charged with the solution SBR. Immediately after completion of SBR charging, the carbon black, ZnO, the antioxidant (such as 6PPD), stearic acid and wax are added. The naphthenic oil is added about a half-minute after completing the addition of carbon black. Once the batch temperature reaches 165°C, the rubber batch is discharged from the mixer.

[0070] In the final mixing batch, the master batch is added to a mixer pre-heated to 70°C to 75°C. The final batch ingredients, as shown in Table 2, are added immediately after adding the master batch to the mixer.

Table 2		
Ingredient	Tread (phr)	Indicator Layer (phr)
4-methylvaleric acid	—	2.0
sulfur	1.5	1.5
TBBS	<u>1.0</u>	<u>1.0</u>
Total (master and final batches):	175.5	177.5

[0071] 4-methylvaleric acid is available from SAFC Flavors and Fragrances Catalog Number W34630-6, FEMA No. 3463, Aldrich Chemical Co. Inc., 6000 N. Teutonia Ave., Milwaukee, WI, 53209. The final batch is discharged when the temperature of the mixture reaches 95°C.

[0072] The tread formula is then extruded to a thickness of 8 mm, while the indicator layer is extruded to a thickness of 1.0 mm to provide an indicator layer component. During construction, the indicator layer component is added to the tire body immediately before adding the tread. Once the indicator layer is added, the tread may be added.

[0073] Unless specifically stated to the contrary, the numerical parameters set forth in the specification, including the attached claims, are approximations that may vary depending on the desired properties sought to be obtained according to the exemplary embodiments. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0074] Furthermore, while the systems, methods, and so on have been illustrated by describing examples, and while the examples have been described in considerable detail, it is not the intention of the applicants to restrict, or in any way, limit the scope of the appended claims to such detail. It is, of course, not possible to describe every conceivable combination of components or methodologies for purposes of describing the systems, methods, and so on provided herein. Additional advantages and modifications will readily appear to those skilled in the art

[0075] Finally, to the extent that the term “includes” or “including” is employed in the detailed description or the claims, it is intended to be inclusive in a manner similar to the term “comprising,” as that term is interpreted when employed as a transitional word in a claim. Furthermore, to the extent that the term “or” is employed in the claims (e.g., A or B) it is intended to mean “A or B or both.” When the applicants intend to indicate “only A or B, but not both,” then the term “only A or B but not both” will be employed. Similarly, when the applicants intend to indicate “one and only one” of A, B, or C, the applicants will employ the phrase “one and only one.” Thus, use of the term “or” herein is the inclusive, and not the exclusive use. See Bryan A. Garner, *A Dictionary of Modern Legal Usage* 624 (2d. Ed. 1995).

CLAIMS

We claim:

1. A pneumatic tire having an indicator of tire wear condition, comprising:
 - a circumferential tread; and
 - a pair of sidewalls extending downwardly from the circumferential tread;
 - a barrier layer located above or outward from an indicator layer;
 - where the indicator layer comprises at least one fragrant chemical; and,
 - where at least one of the tread and sidewalls comprises the barrier layer.
2. The pneumatic tire of Claim 1, where the fragrant chemical comprises microcapsules.
3. The pneumatic tire of Claim 2, where the microcapsules comprise polymeric walls.
4. The pneumatic tire of Claim 3, where the polymeric walls comprises aliphatic or aromatic polysulfide containing between 1 and 6 moles of sulfur per mole of monomer unit.
5. The pneumatic tire of Claim 3, where the polymeric walls comprise a condensation polymer, including at least one of a monomeric unit derived from diol monomer having general structure HO-R'-OH or diacid monomer having general structure HO₂C-R'-CO₂H, where R' has general structure $(\text{CH}_2)_x-\overset{\text{SH}}{\underset{|}{\text{CH}}}-(\text{CH}_2)_y$, and where x and y can range from 1 to about 5, and where the total condensation polymer comprises from 1 to 100 mole per cent R'.
6. The pneumatic tire of Claim 3, where the polymeric wall comprises a condensation polymer comprising at least one of a diol monomer having general structure HO-R'-OH or a diacid monomer having general structure HO₂C-R'-CO₂H, where R' has general structure (CH₂)_x-S_y-(CH₂)_z, and where x and z can range from 1

to about 5 and y can range from 1 to about 6, and where the total condensation polymer comprises from 1 to 100 mole per cent R' .

7. A pneumatic tire having an indicator of elevated tire temperature, comprising:

a circumferential tread portion, a pair of sidewall portions extending downwardly from the circumferential tread, a circumferential belt portion comprising a first and second layer disposed below the tread portion;

where at least one of the tread portion, sidewall portion and circumferential belt portion comprises a tire rubber composition comprising from 0.1 to 20 phr of a thermally-activated fragrant chemical.

8. The pneumatic tire of Claim 7, further comprising at least one belt edge insert beneath the belt portion, and at least one belt wedge between the first and second layer, where the at least one of the belt edge insert or belt wedge comprise between 0.1 and 20 phr of at least one thermally-activated fragrant chemical, and where the at least one thermally-activated fragrant chemical has a melting point between 70° C and 130° C.

9. The pneumatic tire of Claim 7, where the circumferential tread portion or sidewall portion, or both, have between 0.1 and 20 phr of at least one thermally-activated fragrant chemical, and where the at least one thermally activated fragrant chemical has a melting point between 70° and 130° C.

10. A pneumatic tire comprising:

a circumferential tread portion, a pair of sidewall portions each extending downwardly from the circumferential tread to a bead portion, a circumferential belt portion, a circumferential belt portion comprising a first and second layer disposed below the tread portion,

where at least one of the circumferential tread portion, sidewall portions, bead portions, a belt portion comprises a tire rubber composition having from 0.1 to 100 phr of microcapsules containing at least one fragrant chemical.

11. The pneumatic tire of claim 10 further comprising at least one belt edge insert beneath the belt portion, and at least one belt wedge between the first and second layer, at least one of a cap ply disposed above the belt portion, or carcass ply disposed below the belt portion, and an inner liner portion disposed below the belt portion and the at least one of the cap ply and carcass ply;

where at least one of the circumferential tread portion, sidewall portions, bead portions, a belt portion, at least one belt edge insert, at least one belt wedge, at least one of a cap ply or carcass ply, and inner liner portion comprises a tire rubber composition having from 0.1 to 100 phr of microcapsules containing at least one fragrant chemical.

12. A pneumatic tire comprising:

a circumferential tread; and

an interior portion located below the circumferential tread, comprising:

a pair of sidewall portions each extending downwardly from the circumferential tread to a bead portion, a circumferential belt portion, a circumferential belt portion comprising a first and second layer disposed below the tread portion; and,

where at least one of the sidewall portions and bead portions comprises a tire rubber composition having from 0.1 to 100 phr of at least one fragrant chemical.

13. The pneumatic tire of claim 12, where the at least one fragrant chemical is selected from the group consisting essentially of ethers, esters, aldehydes, alcohols, lactones, linear terpenes, cyclic terpenes, amines, aromatics, ketones, thiols, acetals, organic acids, phenols, unsaturated cyclic and acyclic hydrocarbons, and naturally occurring fragrant oils and combinations thereof.

14. The pneumatic tire of claim 12, further comprising,

at least one belt edge insert beneath the belt portion, and at least one belt wedge between the first and second layer, at least one of a cap ply disposed above the belt portion, or carcass ply disposed below the belt

portion, and an inner liner portion disposed below the belt portion and the at least one of the cap ply and carcass ply,

where at least one of the at least one belt edge insert beneath the belt portion, the at least one belt wedge between the first and second layer, the at least one of a cap ply disposed above the belt portion, or carcass ply disposed below the belt portion, and an inner liner portion disposed below the belt portion and the at least one of the cap ply and carcass ply, comprises a tire rubber composition having from 0.1 to 100 phr of at least one fragrant chemical.

15. The pneumatic tire of claim 14, further comprising,

where the at least one of the cap ply carcass ply and belt portion is comprised from at least one of the group consisting essentially of nylon, polyester, aramid, cotton, polynorbornene and rayon fibers and wherein the at least one of the cap ply, carcass ply and belt ply comprises from 0.1% to 10% by weight of at least one fragrant chemical.

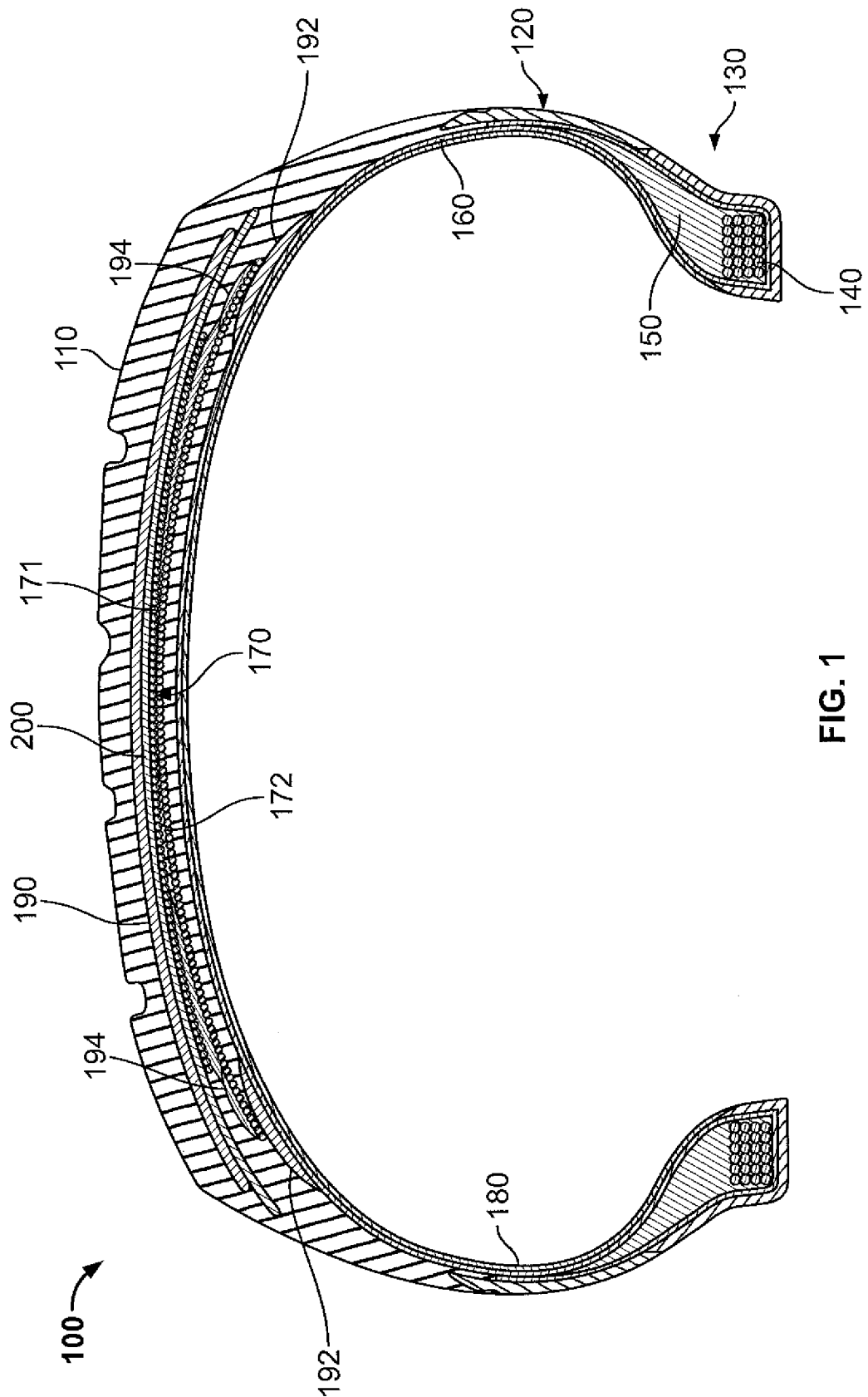


FIG. 1