MULTI-LAYER GOLF BALLS HAVING MOISTURE BARRIER LAYERS BASED ON POLYALKENAMER COMPOSITIONS

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Related U.S. Application Data
Continuation-in-part of application No. 12/358,358, filed on Aug. 12, 2010, which is a continuation-in-part of application No. 10/002,641, filed on Nov. 28, 2001, now Pat. No. 6,547,677, said application No. 12/358,358 is a continuation-in-part of application No. 11/833,601, filed on Aug. 3, 2007, now Pat. No. 7,503,855, which is a continuation of application No. 11/537,830, filed on Oct. 2, 2006, now Pat. No. 7,267,621, which is a continuation of application No. 10/665,176, filed on Sep. 19, 2003, now Pat. No. 7,115,049.

Publication Classification

Abstract
Golf balls having a dual-core comprising an inner core and outer moisture barrier core layer are provided. The outer core help prevent moisture from penetrating into the inner core. A cover layer, preferably made of a polyurethane or polyurea material, is disposed about the outer core layer. The inner and outer cores are formed of a rubber composition, preferably a polyalkenamer rubber. The polyalkenamer rubber composition may further include other rubbers such as polybutadiene, polyisoprene, ethylene propylene rubber, ethylene propylene diene rubber, and styrene-butadiene rubber. The outer core has a moisture vapor transmission rate (MVTR) lower than that of the cover. In one version, the outer core has a MVTR of 1 grams mm/m² day or less, preferably in the range of 0.45 to 0.95 grams mm/m² day.
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CROSS-REFERENCE TO RELATED APPLICATIONS


BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention generally relates to golf balls, and more particularly to golf balls containing dual-layer cores having a large, relatively soft inner core layer surrounded by a thin, relatively hard outer core layer. In one embodiment, the outer core is a moisture barrier layer made of a rubber composition comprising polyalkenamer rubber and preferably polyoctenamer. The moisture barrier layer is disposed about the inner core to prevent moisture from penetrating into the core.

[0004] 2. Brief Review of the Related Art

[0005] Dual- and multi-layer cover golf balls having desirable performance properties, such as spin profile, have been constructed using an ionicomer inner cover layer and a polyurethane outer cover layer. However, there remains a need in the industry for a golf ball construction which provides similar performance properties without requiring more than one cover layer. The present invention provides such golf ball construction, which includes the use of a large, relatively soft inner core layer surrounded by a thin, relatively hard outer core layer, and a cover layer. By eliminating the need for more than one cover layer, while maintaining desirable performance characteristics, golf balls of the present invention provide a viable, cost efficient alternative to current dual- and multi-layer cover golf balls.

[0006] Multi-piece golf balls having solid inner cores made from a polybutadiene rubber material cross-linked with peroxide and/or zinc diacrylate are common in the industry. The core acts as an “engine” for the golf ball and is the primary source of resiliency. One problem with such multi-piece golf balls is that moisture can penetrate into the core and harmfully affect the core’s properties. As the core absorbs water, it tends to lose its resiliency. The compression and coefficient of restitution (COR) of the ball can be reduced significantly if a substantial amount of water enters the core. The golf ball industry has looked to address the problem of moisture penetration by applying a barrier layer over the inner core. The moisture barrier layer surrounds and encapsulates the core to protect it from the negative effects of moisture. Some materials for making moisture barrier layers are described in the patent literature. For example, Cavallaro et al., U.S. Pat. No. 6,632,147 and Hogge et al., U.S. Pat. No. 6,838,028 disclose golf balls having an intermediate moisture vapor barrier layer that may be made from: (i) multi-layer thermoplastic films including polypropylene films that have been metalized or coated with polyvinylidene chloride (PVDC), (ii) blends of ionomers polyvinyl alcohol copolymer and polyamides, and (iii) dispersions of acid salts of polyetheramines, among others.

[0007] Hogge et al., U.S. Pat. No. 6,932,720 discloses golf balls having moisture vapor barrier layers made of butyl rubber. The butyl rubber may be a halogenated butyl rubber such as bromobutyl rubber or chlorobutyl rubber. Also, the butyl rubber may be a sulfonated butyl rubber. The butyl rubber may be blended with other polymers such as double bond-vulcanizable rubber, ethylene propylene diene monomer rubber and vinylidene chloride.

[0008] Hogge et al., U.S. Pat. No. 7,004,854 discloses a golf ball having a core, intermediate barrier layer, and cover. The barrier layer is made of a thermoplastic or thermoset composition comprising micro particles such as fibers, whiskers, metal flakes, micaceous particles, nanoparticles, or combinations thereof. The micro particles are dispersed in a binder such as rubber, polyolefins, styrene polymers, single-site catalyst polyamers, and combinations thereof.

[0009] Hogge et al., U.S. Pat. No. 7,182,702 discloses a golf ball having a moisture vapor barrier layer formed from a composition comprising an elastomer (for example, halogenated butyl rubber) and a double-bond vulcanizable rubber that is cured by infrared or ultraviolet radiation.

[0010] Other materials that can be used in multi-piece golf balls are known in the industry. For example, Kim et al., U.S. Pat. No. 7,528,196 and U.S. Patent Application Publication US 2009/0191981 disclose a golf ball comprising a core, cover layer, and optionally one or more inner cover layers, wherein at least one portion of the ball comprises a blend of a polyalkenamer and polyamide. The polyalkenamer/polyamide composition contains about 2 to about 90 weight % of a polyalkenamer polymer and about 10 to about 98 weight % of a polyamide. The ‘196 patent and ‘981 Published application further disclose that the polyalkenamer/polyamide composition may be blended with other polymers including natural and synthetic rubbers such as polybutadiene, polyisoprene, polychloroprene, polybutylene, and styrene-butadiene rubber prior to molding. However, neither the ‘196 patent nor ‘981 Published application discloses a golf ball having an inner core and surrounding outer core layer, wherein the outer core is a moisture barrier layer that prevents moisture from penetrating into the inner core layer, and the inner core and/or outer core is made of a polyalkenamer rubber composition.

[0011] Although some moisture barrier layers are generally effective at preventing moisture penetration, there is a need for an improved golf ball having a relatively thin moisture barrier layer. The composition needs to be effective at blocking moisture from penetrating into the core, but it also must not degrade the playing performance of the ball. The present
invention provides golf balls having such features as well as other advantageous properties and benefits.

SUMMARY OF THE INVENTION

[0012] In one embodiment, the present invention provides a golf ball comprising an inner core layer, an outer core layer, and a cover layer. The inner core layer has a diameter of from 1.51 inches to 1.58 inches and a compression of 100 or less. The outer core layer has a thickness of from 0.01 inches to 0.06 inches and an outer surface hardness of 80 Shore C or greater. The cover layer has a material hardness of from 30 to 65 Shore D.

[0013] In another embodiment, the present invention provides a golf ball consisting essentially of an inner core layer, an outer core layer, and a cover layer. The inner core layer has a diameter of from 1.51 inches to 1.58 inches and a compression of 100 or less. The outer core layer has a thickness of from 0.01 inches to 0.06 inches and an outer surface hardness of 80 Shore C or greater. The cover layer is formed from a polyurethane- or polyurea-based composition having a material hardness of from 30 to 65 Shore D.

[0014] In another embodiment, the present invention provides a golf ball comprising an inner core layer, an outer core layer, and a cover layer. The inner core layer has a diameter of from 1.51 inches to 1.58 inches and a compression of 100 or less. The outer core layer has a thickness of from 0.01 inches to 0.06 inches and an outer surface hardness of 80 Shore C or greater. The cover layer has a material hardness of from 30 to 65 Shore D. The golf ball does not include a layer formed from an ionomer-based composition.

[0015] In a particularly preferred embodiment, the golf ball contains a dual-core comprising an inner core and outer moisture barrier core layer. The inner core has a diameter of about 1.30 to about 1.58 inches and a compression of about 100 or less, preferably about 70 to about 90. The inner core is made of a first rubber composition and the outer core is made of a second rubber composition comprising a polyalkenamer rubber in an amount of at least 50 weight percent. For example, a polyalkenamer rubber having a trans-content of 55% or greater and a melting point of 30°C or greater can be used to form the outer core. Polyalkenamer rubbers are particularly preferred. The concentration of polyalkenamer rubber is preferably in the range of about 60 to about 100 weight percent based on weight of polymer in the composition. The polyalkenamer rubber helps block moisture from penetrating into the inner core without degrading the playing performance of the ball. The polyalkenamer rubber composition may further include other rubbers such as, for example, polybutadiene, polyisoprene, ethylene propylene rubber, ethylene propylene diene rubber, and styrene-butadiene rubber. The polyalkenamer rubber composition also may be used to make the inner core. The outer core layer helps prevent moisture from penetrating into the inner core and has a thickness of about 0.01 to about 0.20 inches and outer surface hardness of about 80 Shore C or greater. The outer core has a moisture vapor transmission rate (MVTR) lower than that of the cover. In one version, the outer core has a MVTR of 1 grams mm/m²·day or less, preferably in the range of 0.45 to 0.95 grams mm/m²·day, more preferably 0.6 grams mm/m²·day or less, and most preferably 0.4 grams mm/m²·day or less. A cover layer is disposed about the outer core layer and has a material hardness of about 30 to about 65 Shore D in one preferred embodiment. The cover layer may comprise inner and outer cover layers. Preferably, the outer cover layer is formed of a composition comprising a polyurethane; polyurea; or hybrid, blend, or copolymer of polyurethane and polyurea.

[0016] The inner core preferably has a surface hardness of about 75 to about 90, more preferably about 78 to about 87. While the outer core layer preferably has a surface hardness of about 83 to about 97 Shore C and more preferably about 85 to about 93 Shore C. In one version, the inner core has a diameter of about 1.45 to about 1.57 inches and the outer core has a thickness of about 0.025 to about 0.060 inches. In one version, the polyurethane, polyurea, or hybrid polyurethane-polyurea cover layer has a thickness of about 0.10 to about 0.55 inches and preferably 0.10 to 0.40 inches. The polyurethane, polyurea, or polyurethane-polyurea hybrid cover layer has a material hardness of about 40 to about 63 Shore D in one preferred embodiment. In another version, the cover layer comprises inner and outer cover layers, wherein the inner cover has a surface hardness of about 60 Shore D or greater and the outer cover has a surface hardness of about 30 to about 65 Shore D gradient.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The novel features that are characteristic of the present invention are set forth in the appended claims. However, the preferred embodiments of the invention, together with further objects and attendant advantages, are best understood by reference to the following detailed description in connection with the accompanying drawings in which:

[0018] FIG. 1 is a front view of a dimpled golf ball made in accordance with the present invention;

[0019] FIG. 2 is a cross-sectional view of a three-piece golf ball having an inner core, outer moisture barrier core layer comprising a polyalkenamer rubber, and cover made in accordance with the present invention;

[0020] FIG. 3 is a cross-sectional view of a four-piece golf ball having an inner core, outer moisture barrier core layer comprising a polyalkenamer rubber, and inner and outer cover layers made in accordance with the present invention; and

[0021] FIG. 4 is a cross-sectional view of a five-piece golf ball having an inner core, outer moisture barrier core layer comprising the polyalkenamer rubber, intermediate layer, and inner and outer cover layers made in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0022] The present invention relates generally to golf balls containing a core made from a rubber composition, wherein the rubber composition comprises a polyalkenamer, preferably a polyalkenamer. For example, a polyalkenamer rubber having a trans-content of 55% or greater and a melting point of 30°C or greater can be used to form the outer core. Golf balls having various constructions may be made in accordance with this invention. For example, golf balls having three-piece, four-piece, and five-piece constructions with dual-cores and single or multi-layered cover materials may be made. The term, "layer" as used herein means generally any spherical portion of the golf ball. More particularly, in one version, a three-piece golf ball comprising a dual-core having a solid center (otherwise referred to as an inner core) and a surrounding outer core layer and a single-layered cover is made. The outer core layer has moisture barrier properties to protect the inner core and prevent moisture from penetrating therein. In another version, a four-piece ball having a dual-
core and multi-layered cover (having an inner cover layer and outer cover layer) is made. In yet another construction, a five-piece golf ball having a dual-core, intermediate layer, and multi-layered cover is made. The diameter and thickness of the different layers along with properties such as hardness and compression may vary depending upon the construction and desired playing performance properties of the golf ball. The core may contain sections having substantially the same hardness or different hardness levels. That is, there can be substantially uniform hardness throughout the different sections or there can be hardness gradients as discussed in further detail.

In one preferred embodiment, the golf ball contains a large, relatively soft inner core layer surrounded by a thin, relatively hard outer core layer. The large, relatively soft inner core layer has an outer diameter within a range having a lower limit of 1.50 or 1.51 or 1.52 or 1.53 or 1.54 or 1.55 inches and an upper limit of 1.55 or 1.56 or 1.57 or 1.58 inches. The volume of the inner core layer is preferably at least 70%, or at least 75%, or at least 80% of the total volume of the combined inner and outer core layers. The inner core layer has a compression of 100 or less, or less than 100, or 90 or less, or less than 90, or 70 or less, or less than 70, or a compression within a range having a lower limit of 70 or 75 or 80 or 85 and an upper limit of 90 or 95 or 100 or 110. The inner core layer has an outer surface hardness within a range having a lower limit of 50 or 55 or 60 or 65 or 70 or 75 or 78 or 80 Shore C and an upper limit of 80 or 85 or 90 or 95 Shore C, and a center hardness within a range having a lower limit of 40 or 45 or 50 or 55 Shore C and an upper limit of 60 or 65 or 70 Shore C. The inner core layer has a negative hardness gradient, zero hardness gradient, or a positive hardness gradient of up to 45 Shore C.

The thin, relatively hard outer core layer has a thickness within a range having a lower limit of from 0.005 or 0.01 or 0.02 or 0.03 or 0.05 inches and an upper limit of 0.035 or 0.04 or 0.045 or 0.05 or 0.055 or 0.06 inches. The thickness of the outer core layer is preferably such that the dual-layer core has an outer diameter within a range having a lower limit of 1.60 or 1.61 or 1.62 inches and an upper limit of 1.62 or 1.63 or 1.64 inches. The outer core layer has an outer surface Shore C hardness greater than the Shore C hardness of the inner core layer’s outer surface. In one embodiment, the outer core layer has an outer surface hardness of 80 Shore C or greater or 82 Shore C or greater. In another embodiment, the outer core layer has an outer surface hardness within a range having a lower limit of 80 or 82 or 85 Shore C and an upper limit of 90 or 92 or 93 or 95 Shore C. In another embodiment, the outer core layer has an outer surface hardness within a range having a lower limit of 50 or 53 or 55 or 58 Shore D and an upper limit of 60 or 62 or 64 or 70 Shore D. In an alternative embodiment, the thin, relatively hard outer core layer is replaced with a thin, relatively soft and flexible outer core layer having an outer surface hardness of from 50 to 80 Shore C.

For purposes of the present disclosure, a hardness gradient of a golf ball layer is defined by hardness measurements made at the outer surface of the layer and the inner surface of the layer. “Negative” and “positive” refer to the result of subtracting the hardness value at the innermost surface of the golf ball component from the hardness value at the outermost surface of the component. For example, if the outer surface of a solid core has a lower hardness value than the center (i.e., the surface is softer than the center), the hardness gradient will be deemed a “negative” gradient.

In one embodiment, the golf ball contains a dual-core having an inner core and a surrounding outer moisture barrier core layer. The inner core has a “positive” hardness gradient and the outer core layer has a “negative” hardness gradient (that is, the outer surface of the outer core layer is softer than the inner surface of the outer core layer). Other embodiments of golf balls having various combinations of positive, negative, and zero hardness gradients may be made in accordance with this invention. For example, the inner core may have a positive hardness gradient and the outer core layer also may have a positive hardness gradient. In another example, the inner core may have a positive hardness gradient and the outer core layer may have a zero hardness gradient. (That is, the hardness values of the outer surface of the outer core layer and the inner surface of the outer core layer are substantially the same.) Particularly, the term, “zero hardness gradient” as used herein, means a surface to center Shore C hardness gradient of less than 8, preferably less than 5 and most preferably less than 3 and may have a value of zero or negative 1 to negative 25. The term, “negative hardness gradient” as used herein, means a surface to center Shore C hardness gradient of less than negative 1 to negative 25. The term, “positive hardness gradient” as used herein, means a surface to center Shore C hardness gradient of greater than negative 8, preferably greater than 5 and most preferably greater than 3 and most preferably greater than 0. By the term, “steep positive hardness gradient” as used herein, it is meant surface to center Shore C hardness gradient of 20 or greater, more preferably 25 or greater, and most preferably 30 or greater. For example, the core may have a steep positive hardness gradient of 35, 40, or 45 Shore C or greater. Methods for measuring the hardness of the inner core and surrounding layers and determining the hardness gradients are discussed in further detail below. Hardness gradients are disclosed more fully, for example, in U.S. Pat. Nos. 7,429, 221; 7,427,242; 7,410,429; and 7,255,656, the entire disclosures of which are hereby incorporated herein by reference.

The inner and outer core layers are preferably formed from rubber-based compositions. Suitable rubber core compositions include natural and synthetic rubbers including, but not limited to, polybutadiene, polyisoprene, ethylene propylene rubber (“EPR”), styrene-butadiene rubber, styrene block copolymer rubbers (such as SIS, SIB, SBS, SBS, and the like, where “S” is styrene, “I” is isobutylene, and “B” is butadiene), butyl rubber, halobutyl rubber, polyisobutene elastomers, polyethylene elastomers, polyurethane elastomers, polychloroprene elastomers, copolymers of isobutylene and para-alkylstyrene, halogenated copolymers of isobutylen and para-alkylstyrene, copolymers of butadiene with acrylonitrile, polychloroprene, polybutadiene rubber, chlorinated isoprene rubber, acrylonitrile chlorinated isoprene rubber, and combinations of two or more thereof. Dienes rubber are preferred, particularly polybutadiene, styrene-butadiene, and mixtures of polybutadiene with other elastomers wherein the amount of polybutadiene present is at least 40 wt % based on the total polymeric weight of the mixture. Suitable polybutadiene-based and styrene-butadiene-based rubber core compositions preferably comprise the base rubber, an initiator agent, and a coagent. Suitable examples of commercially available polybutadiene include, but are not limited to, Buna CB neodymium catalyzed polybutadiene rubbers, such as Buna CB 23, and Taktene® cobalt catalyzed polybutadiene.
rubbers, such as TakteneR 220 and 221, commercially available from LANXESSR Corporation; Euprene® NEOCISE® BR 40 and BR 60, commercially available from Polimeri Europa®; UBE POL-BR® rubbers, commercially available from UBE Industries, Inc.; BR 01, commercially available from Japan Synthetic Rubber Co., Ltd.; and Neodene neodymium catalyzed high cis polybutadiene rubbers, such as Neodene BR 40, commercially available from Karbochem.

[0028] Suitable initiator agents include organic peroxides, high energy radiation sources capable of generating free radicals, and combinations thereof. High energy radiation sources capable of generating free radicals include, but are not limited to, electron beams, ultra-violet radiation, gamma radiation, X-ray radiation, infrared radiation, heat, and combinations thereof. Suitable organic peroxides include, but are not limited to, dicumyl peroxide; n-buty1-4,4-di(t-buty1peroxy)valerate; 1,1-di(t-buty1peroxy)3,3,5-trimethylcyclohexane; 2,5-dimethyl-2,3-di(t-buty1peroxy)hexane; di-t-buty1 peroxide; di-t-amyl peroxide; t-buty1 peroxide; t-buty1 cumyl peroxide; 2,5-dimethyl-2,3-di(t-buty1peroxy)hexy1ene; 3,4-di(t-buty1-peroxyisopropyl)benzene; dilauroyl peroxide; dibenzoyl peroxide; t-buty1 hydroperoxide; lauryl peroxide; benzoyl peroxide; and combinations thereof. In a particular embodiment, the initiator agent is dicumyl peroxide, including, but not limited to Perkadox® BC, commercially available from Akzo Nobel. Peroxide initiator agents are generally present in the rubber composition in an amount of at least 0.05 parts by weight per 100 parts of the base rubber, or an amount within the range having a lower limit of 0.05 parts or 0.1 parts or 0.25 parts or 1 part or 1.25 parts or 1.5 parts by weight per 100 parts of the base rubber, and an upper limit of 2.5 parts or 3 parts or 5 parts or 6 parts or 10 parts or 15 parts by weight per 100 parts of the base rubber.

[0029] Co-agents are commonly used with peroxides to increase the state of cure. Suitable coagents include, but are not limited to, metal salts of unsaturated carboxylic acids; unsaturated vinyl compounds and polyfunctional monomers (e.g., trimethylolpropane trimethylacrylate); phenylene bismaleimide; and combinations thereof. Particular examples of suitable metal salts include, but are not limited to, one or more metal salts of acrylates, diacrylates, methacrylates, and dimethacrylates, wherein the metal is selected from magnesium, calcium, zinc, aluminum, lithium, nickel, and sodium. In a particular embodiment, the co-agent is selected from zinc salts of acrylates, diallylates, methacrylates, dimethacrylates, and mixtures thereof. In another particular embodiment, the co-agent is zinc diacrylate. When the co-agent is zinc diacrylate and/or zinc dimethacrylate, the co-agent is typically included in the rubber composition in an amount within the range having a lower limit of 1 or 5 or 10 or 15 or 19 or 20 parts by weight per 100 parts of the base rubber, and an upper limit of 24 or 25 or 30 or 35 or 40 or 45 or 50 or 60 parts by weight per 100 parts of the base rubber. When one or more less active co-agents are used, such as zinc monomethacrylate and various liquid acrylates and methacrylates, the amount of the less active co-agent used may be the same as or higher than for zinc diacrylate and zinc dimethacrylate co-agents. The desired composition may be obtained by adjusting the amount of cross-linking, which can be achieved, for example, by altering the type and amount of co-agent.

[0030] The rubber composition optionally includes a curing agent. Suitable curing agents include, but are not limited to, sulfur; N-oxydiethylene 2-benzothiazole sulfenamide; N,N-di-ortho-tolyldiamidine; bismuth dimethylthiocarbamate; N-cyclohexyl 2-benzothiazole sulfenamide; N,N-diphenylguanidine; 4-morpholino-2-benzothiazole disulfide; 2-pentamethylene thiuram hexasulfide; thiuram disulfides; mercaptobenzothiazoles; sulfenamides; dialkylthiocarbamates; thiuram sulfides; guanidines; thioureas; xanthates; thiophosphates; aldehyde-amines; dibenzothiazyl disulfide; tetraethylthiuram disulfide; and combinations thereof.

[0031] The rubber composition optionally contains one or more antioxidants. Antioxidants are compounds that can inhibit or prevent the oxidative degradation of the rubber. Some antioxidants also act as free radical scavengers; thus, when antioxidants are included in the rubber composition, the amount of initiator agent used may be as high or higher than the amounts disclosed herein. Suitable antioxidants include, for example, dihydroquinoline antioxidants, amine type antioxidants, and phenolic type antioxidants.

[0032] The rubber composition may contain one or more fillers to adjust the density and/or specific gravity of the core. Exemplary fillers include precipitated hydrated silica, clay, talc, asbestos, glass fibers, amorphous fibers, mica, calcium metasilicate, zinc sulfate, barium sulfate, zinc sulfide, lithopone, silicates, silicon carbide, diatomaceous earth, polyvinyl chloride, carbonates (e.g., calcium carbonate, zinc carbonate, barium carbonate, and magnesium carbonate), metals (e.g., titanium, tungsten, aluminum, bismuth, nickel, molybdenum, iron, lead, copper, boron, cobalt, beryllium, zinc, and tin), metal alloys (e.g., steel, brass, bronze, boron carbide whiskers, and tungsten carbide whiskers), oxides (e.g., zinc oxide, tin oxide, iron oxide, calcium oxide, aluminum oxide, titanium dioxide, magnesium oxide, and zirconium oxide), particular carbonaceous materials (e.g., graphite, carbon black, cotton flock, natural bitumen, cellulose flock, and leather fiber), microballoons (e.g., glass and ceramic), fly ash, reground (i.e., core material that is ground and recycled), nano-fillers and combinations thereof. The amount of particular material(s) present in the rubber composition is typically within a range having a lower limit of 5 parts or 10 parts by weight per 100 parts of the base rubber, and an upper limit of 50 parts or 50 parts or 100 parts by weight per 100 parts of the base rubber. Filler materials may be dual-functional fillers, such as zinc oxide (which may be used as a filler/acid scavenger) and titanium dioxide (which may be used as a filler/brightener material).

[0033] The rubber composition may also contain one or more additives selected from processing aids, processing oils, plasticizers, coloring agents, fluorescent agents, chemical blowing and foaming agents, defoaming agents, stabilizers, softening agents, impact modifiers, free radical scavengers, accelerators, scorch retarders, and the like. The amount of additive(s) typically present in the rubber composition is typically within a range having a lower limit of 0 parts by weight per 100 parts of the base rubber, and an upper limit of 20 parts or 50 parts or 100 parts or 150 parts by weight per 100 parts of the base rubber.

[0034] The rubber composition optionally includes a soft and fast agent. As used herein, “soft and fast agent” means any compound or a blend thereof that is capable of making a core 1) softer (have a lower compression) at a constant COR and/or 2) faster (have a higher COR) at equal compression, when
compared to a core equivalently prepared without a soft and fast agent. Preferably, the rubber composition contains from 0.05 phr to 10.0 phr of a soft and fast agent. In one embodiment, the soft and fast agent is present in an amount within a range having a lower limit of 0.05 or 0.1 or 0.2 or 0.5 phr and an upper limit of 1.0 or 2.0 or 3.0 or 5.0 phr. In another embodiment, the soft and fast agent is present in an amount of from 2.0 phr to 5.0 phr, or from 2.35 phr to 4.0 phr, or from 2.55 phr to 3.0 phr. In an alternative high concentration embodiment, the soft and fast agent is present in an amount of from 5.0 phr to 10.0 phr, or from 6.0 phr to 9.0 phr, or from 7.0 phr to 8.0 phr. In another embodiment, the soft and fast agent is present in an amount of 2.6 phr.

[0035] Suitable soft and fast agents include, but are not limited to, organosulfur and metal-containing organosulfur compounds; organic sulfur compounds, including mono, di, and poly sulfides, thiol, and mercapto compounds; inorganic sulfide compounds; blends of an organosulfur compound and an inorganic sulfide compound; Group VIA compounds; substituted and unsubstituted aromatic organic compounds that do not contain sulfur or metal; aromatic organometallic compounds; hydroquinones; benzoquinones; quinhydrones; catechols; resorcinsols; and combinations thereof.

[0036] Preferably, the halogenated thio phenol compound is pentachlorothiophenol, which is commercially available in neat form or under the trade name STRUKTOP®, a clay-based carrier containing the sulfur compound pentachlorothiophenol loaded at 45 percent (correlating to 2.4 parts PCTP). STRUKTOP® is commercially available from Struktur Company of America of Stow, Ohio. PCTP is commercially available in neat form from eChinachem of San Francisco, Calif., and in the salt form from eChinachem of San Francisco, Calif. Most preferably, the halogenated thio phenol compound is the zinc salt of pentachlorothiophenol, which is commercially available from eChinachem of San Francisco, Calif. Suitable organosulfur compounds are further disclosed, for example, in U.S. Pat. Nos. 6,635,716, 6,919,393, 7,005,479 and 7,148,279, the entire disclosures of which are hereby incorporated herein by reference. In a particular embodiment, the soft and fast agent is selected from zinc pentachlorothiophenol, pentachlorothiophenol, diethyl disulfide, diphenyl disulfide, dixyl disulfide, 2-nitroresorcinol, and combinations thereof.

[0037] Suitable types and amounts of base rubber, initiator agent, co-agent, filler, and additives are fully described herein, for example, U.S. Pat. Nos. 6,566,483, 6,695,718, and 6,939,907, 7,041,721 and 7,158,460, the entire disclosures of which are hereby incorporated herein by reference. In a particular embodiment, the inner and/or outer core layer composition includes from 1 to 100 phr of a stiffening agent. Preferably, a stiffening agent is present in the outer core layer composition and not the inner core layer composition. Suitable stiffening agents include, but are not limited to, ionomers, acid copolymers and terpolymers, polyamides, and polystyrenes. Stiffening agents are further disclosed, for example, in U.S. Pat. Nos. 6,120,390 and 6,284,840, the entire disclosures of which are hereby incorporated herein by reference. A transpolysisoprene (e.g., TP-301 transpolysisoprene, commercially available from Kuranay Co., Ltd.) or transbutadiene rubber may also be added to increase stiffness to a core layer and/or improve cold-forming properties, which may improve processability by making it easier to mold outer core layer half-shells during the golf ball manufacturing process. When included in a core layer composition, the stiffening agent is preferably present in an amount of from 5 to 10 phr.

[0038] The specific gravity of the outer core layer is preferably the same as, substantially the same as, or greater than the specific gravity of the inner core layer. In a particular embodiment, the specific gravity of the outer core layer is greater than that of the inner core layer, and the outer core layer is formed from a thin dense layer composition. Thin dense layer compositions include those disclosed, for example, in U.S. Pat. No. 6,494,795, the entire disclosure of which is hereby incorporated herein by reference. Also suitable for use as thin dense layer compositions are the thermoplastic materials disclosed in U.S. Pat. Nos. 6,149,555 and 6,152,834, the entire disclosure of which is hereby incorporated herein by reference. In a particular embodiment, the outer core layer is a thin dense layer, preferably having a specific gravity of 1.2 or greater, or 1.5 or greater, or 1.8 or greater, or 2 or greater, and a thickness within the range having a lower limit of 0.001 inches or 0.005 inches or 0.01 inches and an upper limit of 0.02 inches or 0.03 inches or 0.05 inches or 0.06 inches. The thin dense layer is preferably applied to the core as a liquid solution, dispersion, lacquer, paste, gel, melt, etc., such as a loaded or filled natural or non-natural rubber latex, polyurethane, polyurea, epoxy, polyester, any reactive or non-reactive coating or casting material; and then cured, dried or evaporated down to the equilibrium solids level. The thin dense layer may also be formed by compression or injection molding, RIM, casting, spraying, dipping, powder coating, or any means of depositing materials onto the inner core. The thin dense layer may also be a thermoplastic polymer loaded with a specific gravity increasing filler, fiber, flake or particulate, such that it can be applied as a thin coating and meets the preferred specific gravity levels discussed above. One particular example of a thin dense layer, which was made from a soft polybutadiene with tungsten powder using the compression molded method, has a thickness of from 0.021 inches to 0.025 inches, a specific gravity of 1.31, and a Shore C hardness of about 72. For reactive liquid systems, the suitable materials include any material which reacts to form a solid such as epoxies, styrenated polyesters, polyurethanes or polyureas, liquid polybutadienes, silicones, silicate gels, agar gels, etc. Casting, RIM, dipping and spraying are the preferred methods of applying a reactive thin dense layer. Non-reactive materials include any combination of a polymer either in melt or flowable form, powder, dissolved or dispersed in a volatile solvent.

[0039] The dual-layer core is surrounded by a cover having one or more layers. Suitable cover materials include, but are not limited to, ionomer resins and blends thereof (e.g., Surlyn® ionomer resins and DuPont® HPF 1000 and HPF 2000, commercially available from E. I. du Pont de Nemours and Company; loteK® ionomers, commercially available from ExxonMobil Chemical Company; Amplify® JO ionomers of ethylene acrylic acid copolymers, commercially available from The Dow Chemical Company; and Clarix® ionomer resins, commercially available from A. Schulman Inc.); polyurethanes; polyureas; copolymers, blends, and hybrids of polyurethane and polyurea, polyethylene, including, for example, low density polyethylene, linear low density polyethylene, and high density polyethylene; polypropylene; rubber-toughened olefin polymers; acid copolymers, e.g., (meth) acrylic acid, which do not become part of an ionomer
copolymer, plastomers, flexomers; styrene/butadiene/styrene block copolymers; styrene/ethylene-butylene/styrene block copolymers; dynamically vulcanized elastomers; ethylene vinyl acetates; ethylene methyl acrylates; polyvinyl chloride resins; polyamides, amide-ester elastomers, and graft copolymers of ionomer and polyamide, including, for example, Pebax® thermoplastic polyether block amides, commercially available from Arkema Inc; crosslinked transpolyisoprene and blends thereof; polyester-based thermoplastic elastomers, such as Hytrel®, commercially available from E. I. du Pont de Nemours and Company; polyurethane-based thermoplastic elastomers, such as Elastollan®, commercially available from BASF; synthetic or natural vulcanized rubber; and combinations thereof. Suitable cover materials and constructions also include, but are not limited to, those disclosed in U.S. Pat. Nos. 6,117,025, 6,767,940, and 6,960,630, the entire disclosures of which are hereby incorporated herein by reference.

[0040] Ionomer-based compositions, particularly olefin-based ionomers, are known to be useful as a golf ball cover material, and particularly as a golf ball inner cover layer material. Olefin-based ionomers are acid copolymers that normally include α-olefin, such as ethylene and an α,β-ethylenically unsaturated carboxylic acid, such as methacrylic acid, acrylic acid, or maleic acid. Other possible carboxylic acid groups include, for example, crotonic, maleic, fumaric, and itaconic acid. The acid copolymers may optionally contain a softening monomer such as alkyl acrylate and alkyl methacrylate, wherein the alkyl groups have from 1 to 8 carbon atoms. “Low acid” and “high acid” olefin-based ionomers, as well as blends of such ionomers, may be used. In general, low acid ionomers are considered to be those containing 16 wt % or less of carboxylic acid, whereas high acid ionomers are considered to be those containing greater than 16 wt % of carboxylic acid. The acidic group in the olefin-based copolymer is partially or totally neutralized with metal ions such as zinc, sodium, lithium, magnesium, potassium, calcium, manganese, nickel, chromium, copper, or a combination thereof. For example, ionomeric resins having carboxylic acid groups that are neutralized from about 10 percent to about 100 percent may be used. In one embodiment, the acid groups are partially neutralized. That is, the neutralization level is from 10 to 80%, more preferably 20 to 70%, and most preferably 30 to 50%. In another embodiment, the acid groups are highly or fully neutralized. That is, the level of neutralization is from 80 to 100%, more preferably 90 to 100%, and most preferably 95 to 100%.

[0041] However, by the present invention, a novel golf ball construction has been discovered having desirable performance characteristics without the need for more than one cover layer, and particularly without the need for an ionomer-based inner cover layer. Thus, in one embodiment, the present invention provides golf balls which do not include a layer formed from an ionomer-based composition. In embodiments of the present invention wherein the golf ball does include a layer formed from an ionomer-based composition, preferred ionomeric compositions include:

[0042] (a) a composition comprising a “high acid ionomer” (i.e., having an acid content of greater than 16 wt %), such as Surlyn 8150®;

[0043] (b) a composition comprising a high acid ionomer and a maleic anhydride-grafted non-ionicomer polymer (e.g., Fusabond® maleic anhydride-grafted metallocene-catalyzed ethylene-butene copolymers). A particularly preferred blend of high acid ionomer and maleic anhydride-grafted polymer is a 84 wt %/16 wt % blend of Surlyn 8150® and Fusabond®. Blends of high acid ionomers with maleic anhydride-grafted polymers are further disclosed, for example, in U.S. Pat. Nos. 6,992,135 and 6,677,401, the entire disclosures of which are hereby incorporated herein by reference;

[0044] (c) a composition comprising a 50/45/5 blend of Surlyn® 8940/Surlyn® 9650/Nucrel® 960, preferably having a material hardness of from 80 to 85 Shore C;

[0045] (d) a composition comprising a 50/25/25 blend of Surlyn® 8940/Surlyn® 9560/Surlyn® 9110, preferably having a material hardness of about 90 Shore C;

[0046] (e) a composition comprising a 50/50 blend of Surlyn® 8940/Surlyn® 9650, preferably having a material hardness of about 86 Shore C;

[0047] (f) a composition comprising a blend of Surlyn® 7940/Surlyn® 8940, optionally including a melt flow modifier;

[0048] (g) a composition comprising a blend of a first high acid ionomer and a second high acid ionomer, wherein the first high acid ionomer is neutralized with a different cation than the second high acid ionomer (e.g., 50/50 blend of Surlyn® 8150 and Surlyn® 9150), optionally including one or more melt flow modifiers such as an ionomer, ethylene-acid copolymer or ester terpolymer; and

[0049] (h) a composition comprising a blend of a first high acid ionomer and a second high acid ionomer, wherein the first high acid ionomer is neutralized with a different cation than the second high acid ionomer, and from 0 to 10 wt % of an ethylene/unacid/ester ionomer wherein the ethylene/acid/ester ionomer is neutralized with the same cation as either the first high acid ionomer or the second high acid ionomer or a different cation than the first and second high acid ionomers (e.g., a blend of 40-50 wt % Surlyn® 8140, 40-50 wt % Surlyn® 9120, and 0-10 wt % Surlyn® 6320).

[0050] Surlyn 8150®, Surlyn® 8940, and Surlyn® 8140 are different grades of E/MAA copolymer in which the acid groups have been partially neutralized with sodium ions. Surlyn® 9650, Surlyn® 9110, and Surlyn® 9120 are different grades of E/MAA copolymer in which the acid groups have been partially neutralized with zinc ions. Surlyn® 7940 is an E/MAA copolymer in which the acid groups have been partially neutralized with lithium ions. Surlyn® 6320 is a very low modulus magnesium ionomer with a medium acid content. Nucrel® 960 is an E/MAA copolymer resin nominally made with 15 wt % methacrylic acid. Surlyn® ionomers, Fusabond® copolymers, and Nucrel® copolymers are commercially available from E. I. du Pont de Nemours and Company.

[0051] Ionomer cover compositions can be blended with non-ionic thermoplastic resins, particularly to manipulate product properties. Examples of suitable non-ionic thermoplastic resins include, but are not limited to, polyurethane, poly-ester-ether, poly-amide-ether, polyether-urea, thermoplastic polyether block amides (e.g., Pebax® block copolymers, commercially available from Arkema Inc.), styrene-butadiene-styrene block copolymers, styrene(ethylene-butylene)-styrene block copolymers, polyamides, polysters, polyolefins (e.g., polyethylene, polypropylene, ethylene-propylene copolymers, poly(ethylene-ether) copolymers, polyethylene-(meth)acrylate, polyethylene-(meth)acrylic acid, functionalized polymers with maleic
anhydride grafting. Fusabond® functionalized olefins commercially available from E. I. du Pont de Nemours and Company, functionalized polymers with epoxidation, elastomers (e.g., ethylene propylene diene monomer rubber, metalloocene-catalyzed polyolefin) and ground powders of thermoset elastomers. Suitable ionomeric cover materials are further disclosed, for example, in U.S. Pat. Nos. 6,653,382, 6,756,436, 6,894,098, 6,919,393, and 6,953,820, the entire disclosures of which are hereby incorporated by reference.

[0052] Polyurethanes, polyureas, and blends, copolymers, and hybrids of polyurethane/polyurea are particularly suitable for forming cover layers of golf balls of the present invention. When used as cover layer materials, polyurethanes and polyureas can be thermoset or thermoplastic. Thermoset materials can be formed into golf ball layers by conventional casting or reaction injection molding techniques. Thermoplastic materials can be formed into golf ball layers by conventional compression or injection molding techniques.

[0053] Polyurethane cover compositions of the present invention include those formed from the reaction product of at least one polyisocyanate and at least one curing agent. The curing agent can include, for example, one or more diamines, one or more polyols, or a combination thereof. The polyisocyanate can be combined with one or more polyols to form a prepolymer, which is then combined with the at least one curing agent. Suitable polyurethane cover compositions of the present invention also include those formed from the reaction product of at least one polyisocyanate and at least one curing agent or the reaction produce of at least one isocyanate, at least one polyol, and at least one curing agent. Basically, polyurethane compositions contain urethane linkages formed by reacting an isocyanate group (—N—C==O) with a hydroxyl group (OH). Polyurethanes are produced by the reaction of a multi-functional isocyanate with a polyol in the presence of a catalyst and other additives. The chain length of the polyurethane prepolymer is extended by reacting it with a hydroxyl-terminated curing agent. Polyurethane compositions, which are distinct from the above-described polyurethanes, also can be formed. In general, polyurea compositions contain urea linkages formed by reacting an isocyanate group (—N—C==O) with an amine group (NH or NH2). The chain length of the polyurea prepolymer is extended by reacting the prepolymer with an amine curing agent. Hybrid compositions containing urethane and urea linkages also may be produced. For example, a polyurethane/urea hybrid composition may be produced when a polyurethane prepolymer is reacted with an amine-terminated curing agent. The term, "hybrid polyurethane/polyureas" is also meant to encompass blends and copolymers of polyurethanes and polyureas.

[0054] Any method known to one of ordinary skill in the art may be used to combine the polyisocyanate, polyol, and curing agent of the present invention. One commonly employed method, known in the art as a one-shot method, involves concurrent mixing of the polyisocyanate, polyol, and curing agent. This method results in a mixture that is inhomogeneous (more random) and affords the manufacturer less control over the molecular structure of the resultant composition. A preferred method of mixing is known as a prepolymer method. In this method, the polyisocyanate and the polyol are mixed separately prior to addition of the curing agent. This method affords a more homogeneous mixture resulting in a more consistent polymer composition.

[0055] Suitable polyurethanes and polyureas are are further disclosed, for example, in U.S. Pat. Nos. 5,334,673, 5,484,870; 6,476,176; 6,506,851; 6,835,794; 6,867,279; 6,958,379; 6,960,630; 6,964,621; 7,041,769; 7,105,623; 7,131,915; and 7,186,777; the entire disclosures of which are hereby incorporated by reference. The cover compositions may include a flow modifier, such as, but not limited to, Nucrel® acid copolymer resins, and particularly Nucrel® 960. Nucrel® acid copolymer resins are commercially available from E. I. du Pont de Nemours and Company. The cover compositions may also include one or more filler(s), such as the fillers given above for rubber compositions of the present invention (e.g., titanium dioxide, barium sulfate, etc.), and/or additive(s), such as coloring agents, fluorescent agents, whitening agents, antioxidants, dispersants, UV absorbers, light stabilizers, plasticizers, surfactants, compatibility agents, foaming agents, reinforcing agents, release agents, and the like.

[0056] In a particular embodiment, the cover is a single-layer cover, having an overall thickness of 0.02 inches or greater or 0.03 inches or greater or 0.04 inches or greater or a thickness within a range having a lower limit of 0.02 or 0.03 or 0.04 inches and an upper limit of 0.15 inches. In a particular aspect of the embodiment, the single-layer cover is formed from a polyurethane- or polyurea-based composition. In another particular aspect of this embodiment, the cover composition has a material hardness within a range having a lower limit of 30 or 40 or 45 Shore D and an upper limit of 55 or 60 or 65 Shore D. In another particular aspect of this embodiment, the golf ball does not include a layer formed from an ionomeric composition.

[0057] In another particular embodiment, the cover is a dual- or multi-layer cover including an inner or intermediate cover layer formed from an ionomeric composition and an outer cover layer formed from a polyurethane- or polyurea-based composition. In a particular aspect of this embodiment, the ionomeric layer preferably has a Shore D hardness of 65 or less, or a Shore D hardness of less than 65, or a Shore D hardness of from 50 to 65, or a Shore D hardness of from 57 to 60, or a Shore D hardness of 58, and has a thickness of from about 0.015 inches to about 0.100 inches or from about 0.20 inches to about 0.50 inches, and more preferably has a thickness of about 0.035 inches. Preferred ionomers include but are not limited to, those selected from copolymers of a C3 to C8 α,β-ethylenically unsaturated mono- or di-carboxylic acid and ethylene or a C3 to C8, ω-olefin, optionally including a softening monomer. The ionomer is optionally highly neutralized (i.e., at least 70%, or at least 90%, or at least 100%, of the acid moiety thereof are neutralized). Commercially available ionomeric materials suitable for use cover layers of the present invention include, but are not limited to, Styrlyn® ionomer resins and DuPont® IPE 1000 and IPE 2000, commercially available from E. I. du Pont de Nemours and Company; and lotek® ionomers, commercially available from ExxonMobil Chemical Company. Also suitable are blends of ionomers with thermoplastic elastomers. In another particular aspect of this embodiment, the outer cover layer has a thickness of from about 0.015 to about 0.040 inches, or a thickness of from about 0.030 inches to about 0.040 inches, or a thickness of from about 0.20 inches to about 0.35 inches.

[0058] The moisture vapor transmission rate (MVTR) of the outer core layer is important, because this layer is disposed immediately about the inner core. That is, the moisture barrier layer encapsulates and envelopes the inner core. The moisture barrier layer protects the inner core and prevents moisture from penetrating therein. The moisture barrier layer has a moisture vapor transmission rate that is lower than the transmission rate of both the cover and inner core. This means that moisture will penetrate through the cover layer, but the interceding moisture barrier layer will minimize the level of moisture penetrating into the inner core. Preferably, the moisture barrier layer (made up of the polyalkenamer rubber com-
position) has a MVTR of 1 grams mm/m² day or less; and preferably it is in the range of 0.45 to 0.95 grams mm/m² day or less, which is typically the MVTR of an ionomer resin such as SURLYN. More preferably, the MVTR of the moisture barrier layer is 0.6 grams mm/m² day or less, and most preferably 0.4 grams mm/m² day or less. The moisture vapor transmission rate is defined as the mass of moisture vapor that diffuses into a material of a given thickness per unit area per unit time. The test methods for measuring MVTR are described in further detail below.

In the present invention, it has been found that no substantial amount of moisture will pass through the interface between the moisture barrier layer and inner core as compared to a core that does not have the dual layer construction of this invention, when exposed to similar conditions. By encapsulating the core in the moisture barrier layer of this invention, the inner core is protected substantially from liquid and vapor penetration. As a result, the optimum properties of such golf balls (for example, high COR) are not substantially reduced when the balls are stored in humid conditions as opposed to golf balls that do not contain the inventive moisture barrier layer. Under standard humidity conditions for testing, the temperature would be in the range of about 100° to 120°F, and the relative humidity would be in the range of about 70% to about 90% for six weeks.

In accordance with the present invention, it has now been found that rubber compositions comprising “cycloalkene rubber” can be used to provide an effective moisture barrier core layer. Cycloalkene rubber polymers made from one or more cycloalkenes having from 5 to 20, preferably 5 to 15, ring carbon atoms. The cycloalkene rubber (also referred to as polyalkenamer or polyalkenamer rubbers) may be prepared by ring opening metathesis polymerization of one or more cycloalkenes in the presence of organometallic catalysts as is known in the art. Such polymerization methods are disclosed, for example, in U.S. Pat. Nos. 3,492,245 and 3,804,803, the disclosures of which are hereby incorporated by reference. By the term, “cycloalkene rubber” as used herein, it is meant a compound having at least 20 weight % macrocycles (cyclic content). The cyclic and linear portions of the cycloalkene rubber have the following general chemical structures:

![Chemical structure diagram](image)

### Examples of suitable polyalkenamer rubbers

Examples of suitable polyalkenamer rubbers are polypropenamer rubber, polypentenamer rubber, polyoctenamer rubber, polydecenamer rubber and polydodecenamer rubber. Polyalkenamer rubbers are commercially available from Evonik Degussa GmbH of Marl, Germany and sold under the VESTENAMER trade name. The polyalkenamer rubber used in the present invention preferably has a trans-bond content of about 55% or greater and a second heat melting point of about 30°C or greater. More preferably, the cycloalkene rubber has a trans-bond content of 75% or greater and a second heat melting point of 50°C or greater. Furthermore, the polyalkenamer rubber material preferably has a molecular weight of about 80,000 or greater (measured according to GPC); a glass transition temperature (Tg) of about 55°C or less (measured according to ISO 6721 or 4663); a cis-to-trans ratio of double bonds of about 40:60 or preferably about 80:20 (measured according to IR); a Mooney viscosity ML (1+4) 100°C less than about 10 (measured according to DIN 53523 or ASTM-D 1646); a viscosity number J/23°C of about 130 or preferably about 120 ml/g (measured according to ISO 1628-1); and a density of about 0.9 g/cm³ or greater (measured according to DIN 53 479 A or ISO 1183).

The polyalkenamer rubber compound, of and by itself, has relatively high crystallinity. For example, a specific grade of polyalkenamer rubber (VESTENAMER 8012) has a crystallinity of approximately 30% (measured by DSC, second melting.) The ratio of cis double bonds to trans double bonds (cis/trans ratio) in the polymer is significant in determining the degree of crystallinity in the polymer. In general, if the trans-bond content of the polymer is relatively high, the crystallinity and melting point of the polymer is relatively high. That is, as the trans-bond content increases, the crystallinity of the polymer increases. The polyalkenamer rubber, VESTENAMER 8012 has a trans-bond content of about 80%. In accordance with the present invention, it has been found the compression of polyalkenamer rubber cores is reduced and the Coefficient of Restitution (“COR”) of the cores is increased when the rubber composition is cross-linked to a relatively high degree and the composition does not contain a reactive cross-linking co-agent such as zinc diacrylate (ZDA). The polyalkenamer rubber composition may be cured using a conventional curing process such as peroxide-curing, sulfur-curing, and high-energy radiation, and combinations thereof. For example, the composition may be peroxide-cured. When peroxide is added at relatively high amounts (particularly, at least 2.5 and preferably 5.0 phr) and the composition (which if it does not contain a reactive cross-linking co-agent such as ZDA) is cured to cross-link the rubber chains, then the compression of the polyalkenamer
rubber cores is reduced and the COR of the cores is increased. It is believed this phenomenon is due, at least in part, to disrupting the crystalline structure of the polymer by curing and cross-linking the composition in accordance with this invention. While not wishing to be bound by any theory, it is believed the cross-linking causes the tightly packed structures within the mass of polyalkenamer polymer to spread out, thus disrupting the crystallinity of the material. It appears the crystallinity may be partially disrupted and the polymer remains in a partially crystalline state. As a result, the polyalkenamer rubber (which if it does not contain a reactive cross-linking agent such as ZDA) becomes softer and more rubbery and the compression of core samples made from the composition decreases.

[0064] One example of a commercially-available material that can be used in accordance with this invention is VESTENAMER 8012 (trans-bond content of about 80% and a melting point of about 54°C). The material, VESTENAMER 6213 (trans-bond content of about 60% and a melting point of about 30°C) also may be effective.

[0065] In the present invention, it has been found that rubber compositions comprising polyalkenamer rubber are particularly effective. Polyalkenamer rubber compositions can be used to make a core layer that effectively protects the inner core from moisture penetrating therein. As a result, the core and other optimum properties of such golf balls are not substantially reduced when the balls are stored in humid conditions as opposed to golf balls that do not contain the inventive moisture barrier layer. The resulting ball has a relatively high COR allowing it to reach a high velocity when struck by a golf club. Thus, the ball tends to travel a greater distance which is particularly important for driver shots off the tee. Furthermore, the ball has a soft feel that provides the player with a more pleasant sensation when he/she strikes the ball with the club. The player senses more control over the ball as the club face impacts. Furthermore, the soft feel of the ball’s cover allows players to place a spin on the ball and better control its flight pattern which is particularly important for approach shots near the green.

[0066] The polyalkenamer rubber is used in an amount of at least 50% by weight based on total amount of polymer in the rubber composition used to make the core. Preferably, the polyalkenamer rubber is present in an amount of 65 to 100% by weight and more preferably 75 to 100% by weight based on total polymer weight. It is believed that when the concentration of the polyalkenamer rubber is less than 50% by weight, the resiliency of the rubber composition is not significantly improved. In particular versions, the blend may contain a lower concentration of polyalkenamer rubber in the amount of 50%, 55%, 60%, 65%, or 70% and an upper concentration of polyalkenamer in the amount of 75%, 80%, 85%, 90%, or 95%.

[0067] The polyalkenamer rubber may be blended with other rubber and polymeric materials. As described above, these rubber materials include, but are not limited to, polybutadiene, polyisoprene, ethylene propylene rubber (“EPR”), ethylene propylene diene rubber (“EPDM”), styrene-butadiene rubber, styrene block copolymer rubbers (such as SIS, SBS, SB, SBS, SBIS, SEBS, and the like, where “S” is styrene, “I” is isobutylene, “B” is butadiene, and “E” is ethylene), butyl rubber, halobutyl rubber, poly styrene elastomers, polyethylene elastomers, polyurethane elastomers, polyurea elastomers, metalloocene-catalyzed elastomers and plastomers, copolymers of isobutylene and para-alkylstyrene, halogenated copolymers of isobutylene and para-alkylstyrene, copolymers of butadiene with acrylonitrile, polychloroprene, alkyl acrylate rubber, chlorinated isoprene rubber, acrylonitrile chlorinated isoprene rubber, and combinations of two or more thereof. A preferred base rubber is 1,4-polybutadiene having a cis-bond structure of at least 40%, preferably greater than 80%, and more preferably greater than 90%.

[0068] Examples of commercially available polybutadiene rubbers that can be used in accordance with this invention include, but are not limited to, BUNA® CB22 and BUNA® CB23, commercially available from Lanxess Corp.; UBE-POL® 360L and UBEPOL® 150L and UBEPOL-BR rubbers, commercially available from UBE Industries, Ltd. of Tokyo, Japan; KINEX® 7245 and KINEX® 7265, commercially available from Goodyear of Akron, Ohio; SE BR-1220, and BUNA® CB1203G1, CB1220, and CB1221, commercially available from Lanxess Corp.; EUROPRENE® NEO-CIS® BR 40 and BR 60, commercially available from Polimeri Europa; and BR 01, BR 730, BR 735, BR 11, and BR 51, commercially available from Japan Synthetic Rubber Co., Ltd.; and Afdene 45, Afdene 50, Neodene 40, and Neodene 45, commercially available from Karbochem (PTY) Ltd. of Bruma, South Africa.

[0069] As discussed above, the polyalkenamer rubber composition may be cured using a conventional curing process. Suitable curing processes include, for example, peroxide-curing, sulfur-curing, high-energy radiation, and combinations thereof. Preferably, the rubber composition contains a free-radical initiator selected from organic peroxides, high energy radiation sources capable of generating free-radicals, and combinations thereof. In one preferred version, the rubber composition is peroxide-cured. Suitable organic peroxides include, but are not limited to, dicumyl peroxide; n-butyl-4,4-di(t-butylperoxy)valerate; 1,1-di(t-butylperoxy)3,5-trimethylcyclohexane; 2,5-dimethyl-2,5-di(t-butylperoxy)hexane; di-t-butyl peroxide; di-t-amyl peroxide; t-butyl peroxide; t-butyl cumyl peroxide; 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3; di(2-t-butyl-peroxycyclopropyl)benzene; dilauryl peroxide; dibenzoyl peroxide; t-butyl hydroperoxide; and combinations thereof. In a particular embodiment, the free radical initiator is dicumyl peroxide, including, but not limited to Perkadox® BC, commercially available from Akzo Nobel. Peroxide free-radical initiators are generally present in the rubber composition in an amount of at least 0.05 parts by weight per 100 parts of the base rubber, or an amount within the range having a lower limit of 0.05 parts or 0.1 parts or 1 part or 1.25 parts or 1.5 parts or 2.5 parts or 5 parts by weight per 100 parts of the total rubbers, and an upper limit of 2.5 parts or 3 parts or 5 parts or 6 parts or 10 parts or 15 parts by weight per 100 parts of the base rubber. In one preferred version, the peroxide free-radical initiator is present in an amount of at least 2.5 and more preferably 5 parts per hundred (phr).

[0070] The polyalkenamer rubber composition may further include a reactive cross-linking co-agent. Suitable co-agents include, but are not limited to, metal salts of unsaturated carboxylic acids having from 3 to 8 carbon atoms; unsaturated vinyl compounds and polyfunctional monomers (e.g., trimethyl/propene trimethacrylate); phenylene bismaleimide; and combinations thereof. Particular examples of suitable metal salts include, but are not limited to, one or more metal salts of acrylates, diacrylates, methacrylates, and dimethacrylates, wherein the metal is selected from magnesium, sodium, zinc, aluminum, lithium, and nickel. In a par-
In another particular embodiment, the co-agent is selected from zinc salts of acrylates, diacrylates, methacrylates, and dimethacrylates. In a particular embodiment, the agent is zinc diacrylate (ZDA). When the co-agent is zinc diacrylate and/or zinc dimethacrylate, the co-agent is typically included in the rubber composition in an amount within the range having a lower limit of 1 or 5 or 10 or 15 or 19 or 20 parts by weight per 100 parts of the total rubber, and an upper limit of 24 or 25 or 30 or 35 or 40 or 45 or 50 or 60 parts by weight per 100 parts of the total rubber.

Radical scavengers such as a halogenated organosulfur, organic sulfide, or inorganic sulfide compounds may be added to the polyalkenamer rubber composition to increase the COR at a given compression. Preferred halogenated organosulfur compounds include, but are not limited to, pentafluorothiophenol (PCTP) and salts of PCTP such as zinc pentafluorothiophenol (ZnPCTP). Using PCTP and ZnPCTP in golf ball inner cores helps produce softer and faster inner cores. The PCTP and ZnPCTP compounds help increase the resiliency and the coefficient of restitution of the core. In a particular embodiment, the soft and fast layer is selected from ZnPCTP, PCTP, diethyl sulfide, diphenyl sulfide, dioxyl sulfide, 2-nitroresorcinol, and combinations thereof.

The polyalkenamer compositions of the present invention also may include “fillers,” which are added to adjust the density and/or specific gravity of the material. As used herein, the term “fillers” includes any compound or composition that can be used to adjust the density and/or other properties of the subject golf ball. Suitable fillers include, but are not limited to, polymeric or mineral fillers, metal fillers, metal alloy fillers, metal oxide fillers and carbonaceous fillers. Fillers can be in the form of flakes, fibers, fibrils, or powders. Regrind, which is ground, recycled core material (for example, ground to about 30 mesh particle size), can also be used. The amount and type of fillers utilized are governed by the amount and weight of other ingredients in the golf ball, since a maximum golf ball weight of 45.93 g (1.62 ounces) has been established by the United States Golf Association (USGA). Suitable fillers generally have a specific gravity from about 2 to 20. In one preferred embodiment, the specific gravity can be about 2 to 6.

Suitable polymeric or mineral fillers include, for example, precipitated hydrated silica, clay, talc, asbestos, glass fibers, aramid fibers, mica, calcium metasilicate, boron sulfate, zinc sulfate, lithopone, silicates, silicon carbide, diatomaceous earth, polystyrene chloride, carbonates such as calcium carbonate and magnesium carbonate. Suitable metal fillers include titanium, tungsten, aluminum, bismuth, nickel, molybdenum, iron, lead, copper, boron, cobalt, beryllium, zinc, and tin. Suitable metal alloys include steel, brass, bronze, boron carbide whiskers, and tungsten carbide whiskers. Suitable metal oxide fillers include zinc oxide, iron oxide, aluminum oxide, titanium oxide, magnesium oxide, and zirconium oxide. Suitable particulate carbonaceous fillers include graphite, carbon black, cotton flock, natural bitumen, cellulose flock, and leather fiber. Micro balloon fillers such as glass and ceramic, and fly ash fillers can also be used.

As discussed above, the rubber compositions may include antioxidants to prevent the breakdown of the elastomers. In addition, the polyalkenamer rubber compositions may optionally include processing aids such as high molecular weight organic acids and salts thereof. Suitable organic acids are aliphatic organic acids, aromatic organic acids, saturated mono-functional organic acids, unsaturated monofunctional organic acids, multi-unsaturated monofunctional organic acids, and dimerized derivatives thereof. Particular examples of suitable organic acids include, but are not limited to, caprylic acid, caprylic acid, capric acid, lauric acid, stearic acid, behenic acid, erucic acid, oleic acid, linoleic acid, myristic acid, benzoic acid, palmitic acid, phenylacetic acid, naphthalenedioic acid, dimerized derivatives thereof. The organic acids are aliphatic, mono-functional (saturated, unsaturated, or multi-unsaturated) organic acids. Salts of these organic acids may also be employed. The salts of organic acids include the salts of barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, or calcium, salts of fatty acids, particularly stearic, behenic, erucic, oleic, linoleic or dimerized derivatives thereof. It is preferred that the organic acids and salts of the present invention be relatively non-migratory (they do not bloom to the surface of the polymer under ambient temperatures) and non-volatile (they do not volatilize at temperatures required for melt-blending).

Other ingredients such as accelerators (for example, tetra methylthiuram), processing aids, dyes and pigments, wetting agents, surfactants, plasticizers, coloring agents, fluorescent agents, chemical blowing and foaming agents, defoaming agents, stabilizers, softening agents, impact modifiers, antioxidants, antiozonants, as well as other additives known in the art may be added to the rubber composition. The core layers may be formed by mixing and molding the rubber composition using conventional techniques. These cores can be used to make finished golf balls by surrounding the core with cover layer(s) as discussed further below.

Coefficient of restitution (“COR”) and Compression are important properties of the golf balls of this invention. Balls with a higher rebound velocity have a higher COR value. Such golf balls rebound faster, retain more total energy when struck with a club, and have longer flight distance. The compression can affect the ball’s spin rate off the driver and the feel of the ball. The golf balls of the present invention preferably have a COR of at least 0.750 and preferably at least 0.800 and compression of from about 70 to about 110, preferably from 90 to 100. The test methods for measuring COR and compression are described in further detail below.

In addition to the material disclosed above, any of the core or cover layers may comprise one or more of the following materials: thermoplastic elastomer, thermoset elastomer, synthetic rubber, thermoplastic vulcanize, copolymeric ionomer, terpolymeric ionomer, polyurethane, polylefin, polyamide, copolymeric polyamide, polyesters, polyester-amides, polyether-amides, polystyrene, acrylonitrile-butadiene-styrene copolymers, polycarbonate, polycarbonate, polyphenylene ether, impact-modified polyphenylene ether, high impact polystyrene, diallyl phthalate polymer, metallocene-catalyzed polymers, styrene-acrylonitrile (SAN), olefin-modified SAN, acrylonitrile-styrene-acrylonitrile, styrene-maleic anhydride (S/MA) polymer, styrenic copolymer, functionalized styrenic copolymer, functionalized styrenic terpolymer, styrenic terpolymer, cellulose polymer, liquid crystal polymer (LCP), ethylene-propylene diene rubber (EPDM), ethylene-vinyl acetate copolymer (EVA), ethylene propylene rubber (EPR), ethylene vinyl acetate, polyurea, and polysiloxane. Suitable polyamides for use as an additional material in compositions disclosed herein also include resins obtained by: (1) polycondensation of (a) a
dicarboxylic acid, such as oxalic acid, adipic acid, sebacic acid, terephthalic acid, isophthalic acid or 1,4-cyclohexanedicarboxylic acid, with (b) a diamine, such as ethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, or decamethylenediamine, 1,4-cyclohexyl-diamine or m-xylendiamine; (2) a ring-opening polymerization of cyclic lactam, such as ε-caprolactam or 6-laurolactam; (3) polycondensation of an aminoarboxylic acid, such as ε-aminoacproic acid, 9-aminononanoic acid, 11-aminoundecanoic acid or 12-aminododecanoic acid; or (4) copolymerization of a cyclic lactam with a dicarboxylic acid and a diamine. Specific examples of suitable polyamides include Nylon 6, Nylon 66, Nylon 610, Nylon 11, Nylon 12, copolymerized Nylon, Nylon MXD6, and Nylon 46.

[0078] Other preferred materials suitable for use as an additional material in golf ball compositions disclosed herein include SK Chemicals of South Korea; Septon® diblock and triblock copolymers, commercially available from Kuraray Corporation of Kurashiki, Japan; and Kraton® diblock and triblock copolymers, commercially available from Kraton Polymers LLC of Houston, Tex.

[0079] In one embodiment, the outer cover layer comprises a partially- or fully-neutralized ionomer, a polyurethane, polyurea, or copolymer, blend or hybrid polyurethane-polyurea. A preferred outer cover layer is a castable or reaction injection molding polyurethane, polyurea or copolymer, blend, or hybrid thereof having a Shore D hardness of about 40 to about 50. The inner cover layer material may be a partially-neutralized ionomer-based composition containing zinc, sodium or lithium such as SURLYN, 8940, 8945, 9910, 7930, 7940, or blend thereof having a Shore D hardness of about 63 to about 68. In another embodiment of the multi-layer cover, the outer cover layer and inner cover layer materials and thickness are the same but, the hardness range is reversed, that is, the outer cover layer is harder than the inner cover.

[0080] As discussed above, ionomer-based compositions, particularly olefin-based ionomers, are known to be useful as golf ball cover materials, particularly as an inner cover layer, because they can impart desirable hardness to the ball. Olefin-based ionomers are acid copolymers that normally include α-olefin, such as ethylene and an α,β-ethylenically unsaturated carboxylic acid having 3 to 8 carbons, such as methacrylic acid or acrylic acid. Other possible carboxylic acid groups include, for example, crotonic, maleic, fumaric, and itaconic acid. The acid copolymers may optionally contain a softening monomer such as alkyl acrylate and alkyl methacrylate, wherein the alkyl groups have from 1 to 8 carbon atoms. “Low acid” and “high acid” olefin-based ionomers, as well as blends of such ionomers, may be used. In general, low acid ionomers are considered to be those containing 16 wt. % or less of carboxylic acid, whereas high acid ionomers are considered to be those containing greater than 16 wt. % of carboxylic acid. The acidic group in the olefin-based ionomer copolymer is partially or totally neutralized with metal ions such as zinc, sodium, lithium, magnesium, potassium, calcium, manganese, nickel, chromium, copper, or a combination thereof. For example, ionomeric resins having carboxylic acid groups that are neutralized from about 10 percent to about 100 percent may be used. In one embodiment, the acid groups are partially neutralized. That is, the neutralization level is from 10 to 80%, more preferably 20 to 70%, and most preferably 50 to 50%. In another embodiment, the acid groups are highly or fully neutralized. That is, the neutralization level is from 80 to 100%, more preferably 90 to 100%, and most preferably 95 to 100%.

[0081] As also discussed above, the golf balls of this invention may be constructed so they do not include a layer formed from an ionomer-based composition. In such instances, a variety of thermoplastic or thermosetting non-ionomeric-based compositions could be used in the cover or intermediate layers. These compositions include, for example, polyesters; polyamides; polyamide-ethers, and polyamide-esters; polyurethanes, polyureas, and polyurethane-polyurea hybrids; fluoropolymers; non-ionomeric acid polymers, such as E/Y- and E/X/Y-type copolymers, wherein E is an olefin (e.g., ethylene), Y is a carboxylic acid, and X is a softening comonomer such as vinyl esters of aliphatic carboxylic acids, and alkyl alkylacylates; metallocene-catalyzed polymers; polystyrenes; polypropylenes and polyethylenes; polyvinyl chlorides and grafted polyvinyl chlorides; polyvinyl acetates; polycarbonates including polycarbonate/acrylonitrile-butadiene-styrene blends, polycarbonate/polyurethane blends, and polycarbonate/polyester blends; polyvinyl alcohols; polyethers; polyimides, polyetherketones, polyamideimides; and mixtures of any two or more of the above thermoplastic polymers. Compositions disclosed herein can be either foamed or filled with density adjusting materials to provide desirable golf ball performance characteristics. The intermediate layer may have moisture barrier properties as described in U.S. Pat. Nos. 6,632,147, 6,838,028, 6,932,720, 7,004,854, and 7,182,702, the disclosures of which are hereby incorporated by reference.

[0082] The present invention is not limited by any particular process for forming the golf ball layer(s). It should be understood that the layer(s) can be formed by any suitable technique, including injection molding, compression molding, casting, and reaction injection molding.

[0083] When injection molding is used, the composition is typically in a pelletized or granulated form that can be easily fed into the throat of an injection molding machine wherein it is melted and conveyed via a screw in a heated barrel at temperatures of from 150°F to 600°F, preferably from 200°F to 500°F. The molten composition is ultimately injected into a closed mold cavity, which may be cooled, at ambient or at an elevated temperature, but typically the mold is cooled to a temperature of from 50°F to 70°F. After residing in the closed mold for a time of from 1 second to 300 seconds, preferably from 20 seconds to 120 seconds, the core and/or core plus one or more additional core or cover layers is removed from the mold and either allowed to cool at ambient or reduced temperatures or is placed in a cooling fluid such as water, ice water, dry ice in a solvent, or the like.

[0084] When compression molding is used to form a core, the composition is first formed into a preform or slug of material, typically in a cylindrical or roughly spherical shape at a weight slightly greater than the desired weight of the molded core. Prior to this step, the composition may be first extruded or otherwise melted and forced through a die after which it is cut into a cylindrical preform. The preform is then placed into a compression mold cavity and compressed at a mold temperature of from 150°F to 400°F, preferably from 250°F to 400°F, and more preferably from 300°F to 400°F. When compression molding a cover layer, half-shells of the cover layer material are first formed via injection molding. A core is then enclosed within two half-shells, which is then placed into a compression mold cavity and compressed.
Reaction injection molding processes are further disclosed, for example, in U.S. Pat. Nos. 6,083,119, 7,208, 562, 7,281,997, 7,282,169, 7,338,391, the entire disclosures of which are hereby incorporated herein by reference.

Thermoplastic layers herein may be treated in such a manner as to create a positive or negative hardness gradient. In golf ball layers of the present invention wherein a thermosetting rubber is used, gradient-producing processes and/or gradient-producing rubber formulation may be employed.

Golf balls of the present invention will typically have dimple coverage of 60% or greater, preferably 65% or greater, and more preferably 75% or greater. The United States Golf Association specifications limit the minimum size of a competition golf ball to 1.680 inches. There is no specification as to the maximum diameter, and golf balls of any size can be used for recreational play. Golf balls of the present invention can have an overall diameter of any size. The preferred diameter of the present golf balls is from 1.680 inches to 1.800 inches. More preferably, the present golf balls have an overall diameter of from 1.680 inches to 1.760 inches, and even more preferably from 1.680 inches to 1.740 inches.

As discussed above, the polyalkenamer rubber materials of this invention may be used with any type of ball construction known in the art. Such golf ball designs include, for example, three-piece, four-piece, and five-piece designs. Referring to FIG. 1, one version of a golf ball that can be made in accordance with this invention is generally indicated at (10). Various patterns and geometric shapes of dimples (11) can be used to modify the aerodynamic properties of golf ball (10). The dimples (11) can be arranged on the surface of the ball (10) using any suitable method known in the art. Referring to FIG. 2, a three-piece golf ball (12) that can be made in accordance with this invention is illustrated. In this version, the ball (12) includes a dual-core (14) comprising an inner core (14a) and outer moisture barrier core layer (14b) along with a polyurethane cover (16). In FIG. 3, a four-piece golf ball (20) containing a dual-core (22) having inner core (22a) and outer moisture barrier core layer (22b), and multi-layer cover (26) comprising inner cover (26a) and outer cover (26b) is shown. In another embodiment, as shown in FIG. 4, the five-piece golf ball (30) contains a dual-core (32) made up of inner core (32a) and outer moisture barrier core layer (32b). The golf ball (40) further includes an intermediate layer (34) and a multi-layered cover (36) comprising inner cover layer (36a) and outer cover layer (36b).Conventional thermoplastic or thermostet resins such as olefin-based ionomeric copolymers, polyamides, polystyres, polycarbonates, polyolefins, polyurethanes, and polyureas as described above can be used to make the inner and outer cover layers. As used herein, the term, "intermediate layer" means a layer of the ball disposed between the core and cover. The intermediate layer may be considered an outer core layer or inner cover layer or any other layer disposed between the inner core and outer cover of the ball. The intermediate layer also may be referred to as a casing or mantle layer. The intermediate layer may be made of any suitable material known in the art including thermoplastic and thermosetting materials, particularly ionomeric or non-ionomeric materials.

In one version, the intermediate layer comprises highly-neutralized polymers and blends thereof ("HNP"). The acid moieties of the HNPs, typically ethylene-based ionomers, are preferably neutralized greater than about 70%, more preferably greater than about 90%, and most preferably at least about 100%. The HNPs can be also be blended with a second polymer component, which, if containing an acid group, may be neutralized in a conventional manner. The second polymer component, which may be partially or fully neutralized, preferably comprises ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, polyamides, poly carbonate s, polystyres, polyurethan es, and polyureas, thermoplastic elastomers, polybutadiene rubber, balata, metallocene-catalyzed polymers (grafted and non-grafted), single-site polymers, high-crystalline acid polymers, cationic ionomers, and the like. HNP polymers typically have a material hardness of between about 20 and about 80 Shore D.

Hardness. The center hardness of a core is obtained according to the following procedure. The core is gently pressed into a hemispherical holder having an internal diameter approximately slightly smaller than the diameter of the core, such that the core is held in place in the hemispherical portion of the holder while concurrently leaving the geometric central plane of the core exposed. The core is secured in the holder by friction, such that it will not move during the cutting and grinding steps, but the friction is not so excessive that distortion of the natural shape of the core would result. The core is secured such that the parting line of the core is roughly parallel to the top of the holder. The diameter of the core is measured to 90 degrees to this orientation prior to securing. A measurement is also made from the bottom of the holder to the top of the core to provide a reference point for future calculations. A rough cut is made slightly above the exposed geometric center of the core using a band saw or other appropriate cutting tool, making sure that the core does not move in the holder during this step. The remainder of the core, still in the holder, is secured to the base plate of a surface grinding machine. The exposed "rough" surface is ground to a smooth, flat surface, revealing the geometric center of the core, which can be verified by measuring the height from the bottom of the holder to the exposed surface of the core, making sure that exactly half of the original height of the core, as measured above, has been removed to within ±0.004 inches. Leaving the core in the holder, the center of the core is found with a center square and carefully marked and the hardness is measured at the center mark according to ASTM D-2240. Additional hardness measurements at any distance from the center of the core can then be made by drawing a line radially outward from the center mark, and measuring the hardness at any given distance along the line, typically in 2 mm increments from the center. The hardness at a particular distance from the center should be measured along at least two, preferably four, radial arms located 180° apart, or 90° apart, respectively, and then averaged. All hardness measurements performed on a plane passing through the geometric center are performed while the core is still in the holder and without having disturbed its orientation, such that the test surface is constantly parallel to the bottom of the holder, and thus also parallel to the properly aligned foot of the durometer.

The outer surface hardness of a golf ball layer is obtained from the average of a number of measurements taken from opposing hemispheres, taking care to avoid making measurements on the parting line of the core or on surface defects, such as holes or protrusions. Hardness measurements are made pursuant to ASTM D-2240 "Indentation Hardness of Rubber and Plastic by Means of a Durometer." Because of the curved surface, care must be taken to ensure that the golf ball or golf ball subassembly is centered under the durometer.
indentor before a surface hardness reading is obtained. A calibrated, digital durometer, capable of reading to 0.1 hardness units is used for the hardness measurements. The digital durometer must be attached to, and its foot made parallel to, the base of an automatic stand. The weight on the durometer and attack rate confor to ASTM D-2240. Hardness points should only be measured once at any particular geometric location.

In certain embodiments, a point or plurality of points measured along the “positive” or “negative” gradients may be above or below a line fit through the gradient and its outermost and innermost hardness values. In an alternative preferred embodiment, the hardest point along a particular steep “positive” or “negative” gradient may be higher than the value at the innermost portion of the inner core (the geometric center) or outer core layer (the inner surface)—as long as the outermost point (i.e., the outer surface of the inner core) is greater than (for “positive”) or lower than (for “negative”) the innermost point (i.e., the geometric center of the inner core or the inner surface of the outer core layer), such that the “positive” and “negative” gradients remain intact.

As discussed above, the direction of the hardness gradient of a golf ball layer is defined by the difference in hardness measurements taken at the outer and inner surfaces of a particular layer. The center hardness of an inner core and hardness of the outer surface of an inner core in a single-core ball or outer core layer are readily determined according to the test procedures provided above. The outer surface of the inner core layer (or other optional intermediate core layers) in a dual-core ball are also readily determined according to the procedures given herein for measuring the outer surface hardness of a golf ball layer, if the measurement is made prior to surrounding the layer with an additional core layer. Once an additional core layer surrounds a layer of interest, the hardness of the inner and outer surfaces of any inner or intermediate layers can be difficult to determine. Therefore, for purposes of the present invention, when the hardness of the inner or outer surface of a core layer is needed after the inner layer has been surrounded with another core layer, the test procedure described above for measuring a point located 1 mm from an interface is used.

Also, it should be understood that there is a fundamental difference between “material hardness” and “hardness as measured directly on a golf ball.” For purposes of the present invention, material hardness is measured according to ASTM D2240 and generally involves measuring the hardness of a flat “slab” or “button” formed of the material. Surface hardness as measured directly on a golf ball (or other spherical surface) typically results in a different hardness value. The difference in “surface hardness” and “material hardness” values is due to several factors including, but not limited to, ball construction (that is, core type, number of cores and/or cover layers, and the like); ball (or sphere) diameter; and the material composition of adjacent layers. It also should be understood that the two measurement techniques are not linearly related and, therefore, one hardness value cannot easily be correlated to the other. Shore C hardness is measured according to the test methods D-2240 as described above.

Moment of Inertia. Golf balls of the present invention preferably have a Moment of Inertia (“MOI”) of 70-95 g cm²; preferably 75-93 g cm², and more preferably 76-90 g cm². For low MOI embodiments, the golf ball preferably has an MOI of 85 g cm² or less, or 85 g cm² or less. For high MOI embodiments, the golf ball preferably has an MOI of 86 g cm² or greater, or 87 g cm² or greater. MOI is measured on a model MOI-005-104 Moment of Inertia Instrument manufactured by Inertia Dynamics of Collinsville, Conn. The instrument is connected to a PC for communication via a COM port and is driven by MOI Instrument Software Version #1.2.

Compression. As disclosed in Jeff Dalton’s Compression by Any Other Name, Science and Golf IV, Proceedings of the World Scientific Congress of Golf (Eric Thain ed., Routledge, 2002) (“J. Dalton”), several different methods can be used to measure compression, including Atti compression, Riehle compression, load/deflection measurements at a variety of fixed loads and offsets, and effective modulus. For purposes of the present invention, “compression” refers to Atti compression and is measured according to a known procedure, using an Atti compression test device, wherein a piston is used to compress a ball against a spring. The travel of the piston is fixed and the deflection of the spring is measured. The measurement of deflection of the spring does not begin with its contact with the ball; rather, there is an offset of approximately the first 1.25 mm (0.05 inches) of the spring’s deflection. Very low stiffness cores will not cause the spring to deflect by more than 1.25 mm and therefore have a zero compression measurement. The Atti compression tester is designed to measure objects having a diameter of 42.7 mm (1.68 inches); thus, smaller objects, such as golf ball cores, must be shimmed to a total height of 42.7 mm to obtain an accurate reading. Conversion from Atti compression to Riehle (cores), Riehle (balls), 100 kg deflection, 130-10 kg deflection or effective modulus can be carried out according to the formulas given in J. Dalton.

Coefficient of Restitution (“COR”). The COR is determined according to a known procedure, wherein a golf ball or golf ball subassembly (for example, a golf ball core) is fired from an air cannon at two given velocities and a velocity of 125 ft/s is used for the calculations. Ballistic light screens are located between the air cannon and steel plate at a fixed distance to measure ball velocity. As the ball travels toward the steel plate, it activates each light screen and the ball’s time period at each light screen is measured. This provides an incoming transit time period which is inversely proportional to the ball’s incoming velocity. The ball makes impact with the steel plate and rebounds so it passes again through the light screens. As the rebounding ball activates each light screen, the ball’s time period at each screen is measured. This provides an outgoing transit time period which is inversely proportional to the ball’s outgoing velocity. The COR is then calculated as the ratio of the ball’s outgoing transit time period to the ball’s incoming transit time period (COR = V_out/ V_in * T_out/T_in).

EXAMPLE

[0100] The following Example is for illustrative purposes only and is not meant to limit the scope of the invention.

Example 1

[0101] In this Example, a slug of a rubber composition having the formulation described in Table 1 was cured at about 330°F. For about 11 minutes to make a core material. The resulting core had a center hardness of about 68 Shore C and a surface hardness of about 70.5 Shore C. In addition, the core had a compression of about 70 and a COR of about 0.775 @ 125 f/s (1.550 inch diameter solid sphere). When the core was cured at about 350°F. For about 11 minutes, the compression increased to about 90 and the COR increased to about 0.790 @ 125 f/s (1.550 inch diameter solid sphere).

| Table 1 |
|------------------|------------------|
| Core Composition | Concentration     |
|                  | (parts per hundred) |
| Vestene® 8012 - polychloroprene rubber | 100 |
| available from Evonik Degussa GmbH. | |
| Zinc dicarboxylic (ZDA) co-agent | 50 |
| Zinc oxide (ZnO) filler | 6 |
| Trigonox 145 free-radical initiator | 1.5 |
| * peroxide free-radical initiator | |
| available from Akzo Nobel. | |
| Zinc pentachlorothiophenol (ZnPCTP) | 1 |

[0102] As used herein, the term “about,” used in connection with one or more numbers or numerical ranges, should be understood to refer to all such numbers, including all numbers in a range. When numerical lower limits and numerical upper limits are set forth herein, it is contemplated that any combination of these values may be used.

[0103] All patents, publications, test procedures, and other references cited herein, including priority documents, are fully incorporated by reference to the extent such disclosure is not inconsistent with this invention and for all jurisdictions in which such incorporation is permitted.

[0104] While the illustrative embodiments of the invention have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those of ordinary skill in the art without departing from the spirit and scope of the invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein, but rather that the claims be construed as encompassing all of the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those of ordinary skill in the art to which the invention pertains.

We claim:
1. A golf ball, comprising:
a dual-core comprising an inner core and outer moisture barrier core layer, wherein the outer core layer surrounds the inner core, the inner core having a diameter of about 1.30 inches to about 1.58 inches and a compression of about 100 or less, the inner core being formed from a first rubber composition and the outer core layer being formed from a second rubber composition, the second rubber composition comprising a polyalkenamer in an amount of at least 50 weight percent; the outer core layer having a thickness of about 0.01 inches to about 0.20 inches and outer surface hardness of about 80 Shore C or greater, wherein the outer core has a moisture vapor transmission rate lower than that of the cover, and a cover layer surrounding the outer core layer, the cover layer having a material hardness of about 30 to about 65 Shore D.
2. The golf ball of claim 1, wherein the outer core has a moisture vapor transmission rate of 1 grams-mm/m²-day or less.
3. The golf ball of claim 2, wherein the outer core has a moisture vapor transmission rate of 0.45 to 0.95 grams-mm/m²-day.
4. The golf ball of claim 3, wherein the inner core has a compression of 70 to 90.
5. The golf ball of claim 4, wherein the inner core has a surface hardness of 75 to 90 Shore C.
6. The golf ball of claim 5, wherein the inner core has a surface hardness of 78 to 87 Shore C.
7. The golf ball of claim 6, wherein the outer core layer has a surface hardness of 83 to 97 Shore C.
8. The golf ball of claim 7, wherein the outer core layer has a surface hardness of 85 to 93 Shore C.
9. The golf ball of claim 8, wherein the inner core has a thickness of 1.45 to 1.57 inches.
10. The golf ball of claim 9, wherein the outer core layer has a thickness of 0.025 to 0.060 inches.
11. The golf ball of claim 10, wherein the cover layer comprises an inner cover layer and outer cover layer.
12. The golf ball of claim 11, wherein the outer cover layer has a material hardness greater than the material hardness of the inner cover.
13. A golf ball, comprising:
a dual-core comprising an inner core and outer moisture barrier core layer, wherein the outer core layer surrounds the inner core, the inner core having a diameter of about 1.51 inches to about 1.58 inches and a compression of about 100 or less, the inner core being formed from a first rubber composition and the outer core layer being formed from a second rubber composition, the second rubber composition comprising a polyalkenamer in an amount of at least 50 weight percent; the outer core layer having a thickness of about 0.01 inches to about 0.06 inches and outer surface hardness of about 80 Shore C or greater, wherein the outer core has a moisture vapor transmission rate lower than that of the cover, and a cover layer surrounding the outer core layer, the cover layer being formed from a composition comprising polyurethane; polyurea; or a hybrid, copolymer or blend of polyurethane and polyurea and having a material hardness of about 30 to about 65 Shore D.
14. The golf ball of claim 13, wherein the outer core has a moisture vapor transmission rate of 1 grams-mm/m²-day or less.
15. The golf ball of claim 14, wherein the outer core has a moisture vapor transmission rate of 0.45 to 0.95 grams-mm/m²-day.
16. The golf ball of claim 15, wherein the outer core layer has a thickness of 0.010 to 0.055 inches.
17. The golf ball of claim 16, wherein the cover layer has a thickness of 0.020 to 0.040 inches.
18. The golf ball of claim 17, wherein the cover layer has a material hardness of 40 to 63 Shore D.
19. The golf ball of claim 13, wherein the cover layer comprises an inner cover layer and outer cover layer, the inner cover layer being formed from an olefin-based ionomer copolymer and the outer cover layer being formed from a composition comprising polyurethane; polyurea; or a hybrid, copolymer, or blend of polyurethane and polyurea.

20. The golf ball of claim 19, wherein the inner cover has a material hardness of 60 Shore D or greater and the outer cover has a material hardness of 30 to 65 Shore D.