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(54) **GOLF BALL COMPRISING FLUORINATED  
SILANE-TREATED FILLER TO PROMOTE  
MOISTURE RESISTANCE**

(76) Inventors: **Michael J. Sullivan**, Barrington, RI  
(US); **Mark L. Binette**,  
Mattapoisett, MA (US); **Brian**  
**Comeau**, Berkley, MA (US)

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(57) **ABSTRACT**

The invention is directed to a golf ball comprising a core, a cover and optionally an intermediate layer disposed between the core and the cover, wherein at least one of the core, the

intermediate layer and the cover comprises a moisture vapor barrier layer formed from a moisture vapor barrier composition comprising at least one diene rubber and at least one fluorinated silane treated filler. The filler is hydrophobically modified by fluorinated silane, a hydrophobizing material capable of rendering the surfaces of the silica particles suitably hydrophobic. This moisture vapor barrier composition, which may be incorporated in the golf ball prior to molding, protects the encased inner golf ball components from moisture penetration which damages the golf ball and deteriorates desired golf ball characteristics. Such a golf ball preserves and even enhances optimum golf ball properties and desired golf ball characteristics such as high spin, resilience and durability which may be negatively influenced or impacted by unintended changes in golf ball component compression, COR and hardness due to moisture invasion. The golf ball may comprise an untreated region and a treated outer surface, the treated outer surface having a moisture vapor transmission rate X and the untreated region having a moisture vapor transmission rate Y, the treated outer surface being treated with and comprising a moisture vapor barrier composition formed from at least one diene rubber and at least one fluorinated silane treated filler such that  $X < Y$ .

# **GOLF BALL COMPRISING FLUORINATED SILANE-TREATED FILLER TO PROMOTE MOISTURE RESISTANCE**

## **FIELD OF THE INVENTION**

**[0001]** Golf balls incorporating materials which protect the golf ball's inner layers and stabilize the golf ball with respect to moisture exposure and absorption.

## **BACKGROUND OF THE INVENTION**

**[0002]** Solid core golf balls are well known in the art. Typically, the core is made from polybutadiene rubber material, which provides the primary source of resiliency for the golf ball. It is also known in the art that increasing the cross-link density of polybutadiene can increase the resiliency of the core. The core is typically protected by a cover from repeated impacts from the golf clubs. The golf ball may comprise additional layers, which can be an outer core layer or an inner cover layer—often to increase the resiliency of the ball.

**[0003]** A known drawback of polybutadiene cores cross-linked with peroxide and/or zinc diacrylate is that moisture adversely affects this material. Water moisture vapor reduces the resiliency of the core and degrades its properties. A polybutadiene core will absorb water and lose its resilience. Thus, preferably a golf ball core is covered quickly to maintain and preserve optimum golf ball properties. The cover is typically made from ionomer resins, balata, and urethane, among other materials. The ionomer covers, particularly the harder ionomers, offer some protection against penetration of water vapor. However, it is more difficult to control or impart spin to balls with hard covers. Conventional urethane covers, on the other hand, while providing better ball control due to increased spin, offer less resistance to water vapor than ionomer covers.

**[0004]** Prolonged exposure to high humidity and elevated temperature may be sufficient to allow water vapor to invade and permeate the cores of some commercially available golf balls. For example at 110° F. and 90% humidity for a sixty day period, significant amounts of moisture enter the cores and reduce the initial velocity of the balls by 1.8 ft/s to 4.0 ft/s or greater. The change in compression may vary from 5 to about 10 or greater. The absorbed water vapor also reduces the coefficient of restitution (COR) of the ball.

**[0005]** Several patents have addressed the water vapor absorption problem. Commonly owned U.S. Pat. No. 7,695,381 takes advantage of the beneficial properties of clays, describing golf balls incorporating a moisture barrier layer in the form of nanocomposite compositions including a thermoplastic polymer and an intercalated clay, the clay being organically modified through a reaction with at least one surfactant. Commonly owned U.S. Pat. No. 7,306,528 discloses golf balls incorporating a thin vapor barrier layer of a copolymer of ethylene and methacrylic acid and/or acrylic acid. Meanwhile, commonly owned U.S. Pat. No. 6,632,147 B2 describes a barrier layer comprising nanoparticles, flaked glass, leafing or non-leafing metal flakes (e.g., aluminum flakes, iron oxide flakes, copper flakes, bronze flakes) or ceramic particles to increase the layer's resistance to the transmission of moisture through the layer. The primary ingredient of the barrier layer is made from a material or composition, such as polybutadiene, natural rubber, butyl-based rubber, acrylics, trans-polyisoprene, neoprene, chlorinated polyethylene, and balata. Furthermore, in one example,

the intermediate layer is made from a multi-layer thermoplastic film having a base layer and a coating layer. The base layer includes polyethylene terephthalate, polybutylene terephthalate, polyethylene naphthalate, polycyclohexanedimethylene terephthalate, and polyethylene naphthalate bibenzoate and the coating layer includes polyvinylidene chloride, ethylene vinyl alcohol, modified polyester, silicon oxide, and one or more copolyesters prepared from dicarboxylic acids and diols or its derivatives. The vapor barrier layer can also have high specific gravity to form a ball with high moment of inertia.

**[0006]** Commonly owned U.S. Pat. No. 5,820,488 discloses a golf ball with a solid inner core, an outer core, and a water vapor barrier layer disposed there between. The water vapor barrier layer can be a polyvinylidene chloride (PVDC) layer or a vermiculite layer. Commonly owned U.S. Pat. Nos. 5,885,172 and 6,132,324 disclose, among other things, a golf ball with a polybutadiene or wound core with an ionomer resin inner cover and a relatively soft urethane outer cover. The hard ionomer inner cover offers some resistance to water vapor penetration and the soft outer cover provides the desirable ball control. These references are incorporated herein by reference in their entireties.

**[0007]** However, there is a need for golf balls incorporating hydrophobic fillers as protective encasing layers and/or coatings which may be added to the layer prior to molding in order to impart moisture penetration resistance to the molded layer thereby preserving, maintaining and/or enhancing optimum golf ball properties and desired golf ball characteristics such as spin, resilience and durability.

## **SUMMARY OF THE INVENTION**

**[0008]** The present invention is directed to a golf ball comprising a core, a cover and optionally an intermediate layer disposed between the core and the cover, wherein at least one of the core, the intermediate layer and the cover comprises a moisture vapor barrier layer formed from a moisture vapor barrier composition comprising at least one diene rubber and at least one fluorinated silane treated filler. Fluorinated silane, a hydrophobizing material, modifies the filler, rendering the surfaces of the silica particles suitably hydrophobic. This moisture vapor barrier composition may be incorporated in the golf ball prior to molding. In a golf ball of the invention, the moisture vapor barrier layer and/or coating protects encased golf ball components from moisture penetration, thereby preserving the golf ball's compression, COR and hardness in order to achieve desired golf ball characteristics such as spin, resilience and durability.

**[0009]** In another embodiment of the invention, at least one of the intermediate layer and the cover is formed from a moisture vapor barrier composition comprising at least one diene rubber and at least one fluorinated silane treated filler. In yet another embodiment, the intermediate layer only is formed from a moisture vapor barrier composition comprising at least one diene rubber and at least one fluorinated silane treated filler. In still another embodiment, the cover layer only is formed from a moisture vapor barrier composition comprising at least one diene rubber and at least one fluorinated silane treated filler. Alternatively, the core only may be formed from a moisture vapor barrier composition comprising at least one diene rubber and at least one fluorinated silane treated filler.

**[0010]** A golf ball of the invention may comprise a core, a cover and a moisture barrier layer disposed between the core and the cover, wherein the moisture vapor barrier layer has a

moisture vapor transmission rate that is lower than that of the cover and the moisture vapor barrier layer is formed from a vapor barrier composition comprising at least one diene rubber and at least one fluorinated silane treated filler.

**[0011]** The golf ball may comprise a core and a cover disposed about the core, wherein the core comprises an inner core region and an outer core region, the outer core region having a moisture vapor transmission rate that is lower than that of the inner core region, wherein the outer core region is formed from a moisture vapor barrier composition comprising at least one diene rubber and at least one fluorinated silane treated filler.

**[0012]** The golf ball may comprise a core and a cover disposed about the core, wherein the core comprises an inner core region and an outer core region, said inner core region having a moisture vapor transmission rate  $X$  and the outer core region having a moisture vapor transmission rate  $Y$ , the outer core region comprising a moisture vapor barrier composition formed from at least one diene rubber and at least one fluorinated silane treated filler such that  $X > Y$ .

**[0013]** In one embodiment,  $Y \leq 0.5X$ . In another embodiment,  $Y \leq 0.3X$ . In yet another embodiment,  $Y \leq 0.15X$ . In still another embodiment,  $Y \leq 0.85X$ . In other embodiments,  $Y \leq 0.75X$ , or  $Y \leq 0.65X$ , or  $Y \leq 0.55X$ , or  $Y \leq 0.45X$ , or  $Y \leq 0.35X$ .  $Y$  may also be equal to or less than about  $0.95X$ .

**[0014]** The golf ball may comprise a core, a cover and an intermediate layer disposed between the core and the cover, wherein the intermediate layer comprises an inner layer and an outer layer, the outer layer having a moisture vapor transmission rate that is lower than that of the inner layer, wherein the outer layer is formed from a moisture vapor barrier composition comprising at least one diene rubber and at least one fluorinated silane treated filler.

**[0015]** The golf ball may comprise a core, a cover and an intermediate layer disposed between the core and the cover, wherein the intermediate layer comprises an inner layer and an outer layer, said inner layer having a moisture vapor transmission rate  $X$  and the outer layer having a moisture vapor transmission rate  $Y$ , the outer layer comprising a moisture vapor barrier composition formed from at least one diene rubber and at least one fluorinated silane treated filler such that  $X > Y$ .

**[0016]** In one embodiment,  $Y \leq 0.5X$ . In another embodiment,  $Y \leq 0.25X$ . In yet another embodiment,  $Y \leq 0.10X$ . In still another embodiment,  $Y \leq 0.85X$ . In other embodiments,  $Y \leq 0.75X$ , or  $Y \leq 0.65X$ , or  $Y \leq 0.55X$ , or  $Y \leq 0.45X$ , or  $Y \leq 0.35X$ .  $Y$  may also be equal to or less than about  $0.95X$ .

**[0017]** The golf ball may alternatively comprise a core and a cover disposed about the core, wherein the cover comprises an inner cover layer and an outer cover layer, said outer cover layer having a moisture vapor transmission rate that is lower than that of the inner cover layer, wherein the outer cover layer is formed from a moisture vapor barrier composition comprising at least one diene rubber and at least one fluorinated silane treated filler.

**[0018]** The golf ball may alternatively comprise a core and a cover disposed about the core, wherein the cover comprises an inner cover layer and an outer cover layer, said inner cover layer having a moisture vapor transmission rate  $X$  and the outer cover layer having a moisture vapor transmission rate  $Y$ , the inner cover layer comprising a moisture vapor barrier composition formed from at least one diene rubber and at least one fluorinated silane treated filler such that  $X < Y$ .

**[0019]** In one embodiment,  $X \leq 0.5Y$ . In another embodiment,  $X \leq 0.25Y$ . In yet another embodiment,  $X \leq 0.10Y$ . In still another embodiment,  $X \leq 0.85Y$ . In other embodiments,  $X \leq 0.75Y$ , or  $X \leq 0.65Y$ , or  $X \leq 0.55Y$ , or  $X \leq 0.45Y$ , or  $X \leq 0.35Y$ .  $X$  may also be equal to or less than about  $0.95Y$ .

**[0020]** The golf ball may alternatively comprise a core and a cover disposed about the core, wherein the cover comprises an inner cover layer and an outer cover layer, said inner cover layer having a moisture vapor transmission rate  $X$  and the outer cover layer having a moisture vapor transmission rate  $Y$ , the outer cover layer comprising a moisture vapor barrier composition formed from at least one diene rubber and at least one fluorinated silane treated filler such that  $X > Y$ .

**[0021]** In one embodiment,  $Y \leq 0.5X$ . In another embodiment,  $Y \leq 0.25X$ . In yet another embodiment,  $Y \leq 0.10X$ . In still another embodiment,  $Y \leq 0.85X$ . In other embodiments,  $Y \leq 0.75X$ , or  $Y \leq 0.65X$ , or  $Y \leq 0.55X$ , or  $Y \leq 0.45X$ , or  $Y \leq 0.35X$ .  $Y$  may also be equal to or less than about  $0.95X$ .

**[0022]** A golf ball of the invention may also comprise a core comprising an untreated region and a treated outer surface, the treated outer surface having a first moisture vapor transmission rate and the untreated region having a second moisture vapor transmission rate, the treated outer surface being treated with and comprising a moisture vapor barrier composition formed from at least one diene rubber and at least one fluorinated silane treated filler such that the first moisture vapor transmission rate is lower than the second moisture vapor transmission rate. Herein, the term "treated" includes but is not limited to coated, rolled, dipped, soaked, sprayed, dusted, wiped or otherwise exposed to the moisture vapor barrier composition.

**[0023]** The golf ball may comprise an untreated region and a treated outer surface, the treated outer surface having a moisture vapor transmission rate  $X$  and the untreated region having a moisture vapor transmission rate  $Y$ , the treated outer surface being treated with and comprising a moisture vapor barrier composition formed from at least one diene rubber and at least one fluorinated silane treated filler such that  $X < Y$ .

**[0024]** In one embodiment,  $X \leq 0.5Y$ . In another embodiment,  $X \leq 0.25Y$ . In yet another embodiment,  $X \leq 0.10Y$ . In still another embodiment,  $X \leq 0.85Y$ . In other embodiments,  $X \leq 0.75Y$ , or  $X \leq 0.65Y$ , or  $X \leq 0.55Y$ , or  $X \leq 0.45Y$ , or  $X \leq 0.35Y$ .  $X$  may also be equal to or less than about  $0.95Y$ .

**[0025]** In any or all of the embodiments herein, the region or layer may alternatively consist essentially of a moisture vapor barrier layer formed from a moisture vapor barrier composition comprising at least one diene rubber and at least one fluorinated silane treated filler. Also, in any or all of the embodiments herein, the region or layer may alternatively consist of a moisture vapor barrier layer formed from a moisture vapor barrier composition comprising at least one diene rubber and at least one fluorinated silane treated filler.

**[0026]** The filler may be selected from the group comprising silica, carbon black, graphite, nano graphite, carbon nanotubes and carbon nanoflakes. In one embodiment, the silica is precipitated silica. The filler may further comprise at least one of a non-fluorinated silane treated silica, fibers, flakes, and a sulfur-comprising organosilicon composition.

**[0027]** In one embodiment, the filler is present in the moisture vapor barrier composition in an amount of from about 1 phr to about 100 phr. In another embodiment, filler is present in the moisture vapor barrier composition in an amount of from about 10 phr to about 80 phr. In yet another embodiment, filler is present in the moisture vapor barrier composition in

an amount of from about 10 phr to about 60 phr. In still another embodiment, filler is present in the moisture vapor barrier composition in an amount of from about 1 phr to about 40 phr. Alternatively, filler is present in the moisture vapor barrier composition in an amount of from about 10 phr to about 25 phr. The filler may also be present in an amount of about 3 phr or even up to about 15 phr.

**[0028]** In one embodiment, the moisture vapor barrier composition is present in at least one of the core, intermediate layer, cover and cover coating in an amount of at least about 3 wt %. In another embodiment, the moisture vapor barrier composition is present in at least one of the core, intermediate layer, cover and cover coating in an amount of about 3 wt % or greater. In yet another embodiment, the moisture vapor barrier composition is present in at least one of the core, intermediate layer, cover and cover coating in an amount of from about 15 wt % to about 90 wt %. In still another embodiment, the moisture vapor barrier composition is present in at least one of the core, intermediate layer, cover and cover coating in an amount of from about 30 wt % to about 75 wt %. The moisture vapor barrier composition may alternatively be present in at least one of the core, intermediate layer, cover and cover coating in an amount of from about 45 wt % to about 65 wt %.

**[0029]** Non-limiting examples of the diene rubber comprise high cis polybutadiene rubber and ethylene propylene diene monomer rubber. The diene rubber may comprise a blend of high cis polybutadiene rubber and at least one different rubber selected from the group comprising natural rubber, balata, trans polyisoprene, styrene butadiene rubber, ethylene propylene rubber, ethylene propylene diene monomer rubber, butyl rubber, halo-butyl rubber, low-cis polybutadiene rubber, and trans polybutadiene rubber.

**[0030]** The ratio of high cis polybutadiene rubber to the at least one different rubber may be from about 9:1 to about 1:9. In another embodiment, the ratio of high cis polybutadiene rubber to the at least one different rubber may be from about 1:4 to about 4:1. In yet another embodiment, the ratio of high cis polybutadiene rubber to the at least one different rubber is from about 2:3 to about 3:2. In still another embodiment, the ratio of high cis polybutadiene rubber to the at least one different rubber is from about 1:7 to about 7:1. The ratio of high cis polybutadiene rubber to the at least one different rubber may also be from about 2:5 to about 5:2.

**[0031]** The high-cis polybutadiene rubber may be cobalt-catalyzed, nickel-catalyzed, lithium-catalyzed, or neodymium-catalyzed.

**[0032]** In one embodiment, the moisture vapor barrier composition has a moisture vapor transmission rate of up to about 15% greater than that of an ionomer resin. In another embodiment, the moisture vapor barrier composition has a moisture vapor transmission rate of from about 0.45 grams mm/m<sup>2</sup> day to about 1.5 grams mm/m<sup>2</sup> day. In yet another embodiment, the moisture vapor barrier composition has a moisture vapor transmission rate of about 0.95 grams mm/m<sup>2</sup> day or greater.

**[0033]** The moisture vapor barrier composition may have a Mooney viscosity of from about 25 to about 125. In another embodiment, the moisture vapor barrier composition has a Mooney viscosity of from about 30 to about 100. In yet another embodiment, the moisture vapor barrier composition has a Mooney viscosity of from about 40 to about 60. In still another embodiment, the moisture vapor barrier composition

has a Mooney viscosity of from about 40 to about 90. The measurement of Mooney viscosity is defined according to ASTM D-1646.

**[0034]** In one embodiment, the overall golf ball has a compression of from about 25 to about 110. In another embodiment, the overall golf ball has a compression of from about 35 to about 100. In yet another embodiment, the overall golf ball has a compression of from about 45 to about 95. In still another embodiment, the compression may be from about 55 to about 85, or from about 65 to about 75. Meanwhile, the compression may also be from about 50 to about 110, or from about 60 to about 100, or from about 70 to about 90, or even from about 80 to about 110.

**[0035]** Generally, in golf balls of the invention, the overall golf ball COR is at least about 0.780. In another embodiment, the overall golf ball COR is at least about 0.788. In yet another embodiment, the overall golf ball COR is at least about 0.791. In still another embodiment, the overall golf ball COR is at least about 0.794. Also, the overall golf ball COR may be at least about 0.797. The overall golf ball COR may even be at least about 0.800, or at least about 0.803, or at least about 0.812.

#### DETAILED DESCRIPTION

**[0036]** The moisture vapor transmission rate as used herein is defined as the mass of moisture vapor that diffuses into a material of a given thickness per unit area per unit time. The preferred standards of measuring the moisture vapor transmission rate include ASTM F1249-90 entitled "Standard Test Method for Water Vapor Transmission Rate Through Plastic Film and Sheeting Using a Modulated Infrared Sensor," and ASTM F372-94 entitled "Standard Test Method for Water Vapor Transmission Rate of Flexible Barrier Materials Using an Infrared Detection Technique," among others.

**[0037]** Suitable polybutadiene rubbers for blending with the base rubber may include BUNA® CB22, BUNA® CB23 and BUNA® CB24, BUNA® 1203G1, 1220, 1221, and BUNA® CBNd-40, commercially available from LANXESS Corporation; BSTE BR-1220 available from BST Elastomers Co. LTD; UBEPOL® 360L and UBEPOL® 150L and UBEPOL-BR rubbers, commercially available from UBE Industries, Ltd. of Tokyo, Japan; Budene 1207, 1208 and 1280, commercially available from Goodyear of Akron, Ohio; SE BR-1220, commercially available from Dow Chemical Company; Europrene® NEOCIS® 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 KARBOCHEM® Neodene 40, 45, and 60, commercially available from Karbochem.

**[0038]** The base rubber may further include polyisoprene rubber, natural rubber, ethylene-propylene rubber, ethylene-propylene diene rubber, styrene-butadiene rubber, and combinations of two or more thereof. Another preferred base rubber is polybutadiene optionally mixed with one or more elastomers such as polyisoprene rubber, natural rubber, ethylene propylene rubber, ethylene propylene diene rubber, styrene-butadiene rubber, polystyrene elastomers, polyethylene elastomers, polyurethane elastomers, polyurea elastomers, acrylate rubbers, polyoctenamers, metalloctene-catalyzed elastomers, and plastomers. As discussed further below, highly neutralized acid copolymers (HNPs), as known in the art, also can be used to form the core layer as part of the blend. Such compositions will provide increased flexural modulus

and toughness thereby improving the golf ball's performance including its impact durability.

**[0039]** The base rubber typically is mixed with at least one reactive cross-linking co-agent to enhance the hardness of the rubber composition. Suitable co-agents include, but are not limited to, unsaturated carboxylic acids and unsaturated vinyl compounds. A preferred unsaturated vinyl compound is trimethylolpropane trimethacrylate. The rubber composition is cured using a conventional curing process. Suitable curing processes include, for example, peroxide curing, sulfur curing, high-energy radiation, and combinations thereof. In one embodiment, the base rubber is peroxide cured. Organic peroxides suitable as free-radical initiators include, for example, dicumyl peroxide; n-butyl-4,4-di(t-butylperoxy) valerate; 1,1-di(t-butylperoxy)3,3,5-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-butylperoxyisopropyl)benzene; dilauroyl peroxide; dibenzoyl peroxide; t-butyl hydroperoxide; and combinations thereof. Cross-linking agents are used to cross-link at least a portion of the polymer chains in the composition. Suitable cross-linking agents include, for example, metal salts of unsaturated carboxylic acids having from 3 to 8 carbon atoms; unsaturated vinyl compounds and polyfunctional monomers (for example, trimethylolpropane trimethacrylate); phenylene bismaleimide; and combinations thereof. In a particular embodiment, the cross-linking agent is selected from zinc salts of acrylates, diacrylates, methacrylates, and dimethacrylates. In another particular embodiment, the cross-linking agent is zinc diacrylate ("ZDA"). Commercially available zinc diacrylates include those selected from Cray Valley Resource Innovations Inc.

**[0040]** Other elastomers known in the art may also be added, such as other polybutadiene rubbers, natural rubber, styrene butadiene rubber, and/or isoprene rubber in order to further modify the properties of the core. When a mixture of elastomers is used, the amounts of other constituents in the core composition are typically based on 100 parts by weight of the total elastomer mixture.

**[0041]** Thermoplastic elastomers (TPE) may also be used to modify the properties of the core layers, or the uncured core layer stock by blending with the base thermoset rubber. These TPEs include natural or synthetic balata, or high trans-polyisoprene, high trans-polybutadiene, or any styrenic block copolymer, such as styrene ethylene butadiene styrene, styrene-isoprene-styrene, etc., a metallocene or other single-site catalyzed polyolefin such as ethylene-octene, or ethylene-butene, or thermoplastic polyurethanes (TPU), including copolymers, e.g. with silicone. Other suitable TPEs for blending with the thermoset rubbers of the present invention include PEBAX®, which is believed to comprise polyether amide copolymers, HYTREL®, which is believed to comprise polyether ester copolymers, thermoplastic urethane, and KRATON®, which is believed to comprise styrenic block copolymers elastomers. Any of the TPEs or TPUs above may also contain functionality suitable for grafting, including maleic acid or maleic anhydride. Any of the Thermoplastic Vulcanized Rubbers (TPV) such as Santoprene® or Vibram® or ETPV® can be used along with a present invention. In one embodiment, the TPV has a thermoplastic as a continuous phase and a cross-linked rubber particulate as a dispersed (or discontinuous) phase. In another embodiment, the TPV has a cross-linked phase as a continuous phase and a thermoplastic

as a dispersed (or discontinuous) phase to provide reduced loss in elasticity in order to improve the resiliency of the golf ball.

**[0042]** The rubber compositions also may contain "soft and fast" agents such as a halogenated organosulfur, organic disulfide, or inorganic disulfide compounds. Particularly suitable halogenated organosulfur compounds include, but are not limited to, halogenated thiophenols. Preferred organic sulfur compounds include, but not limited to, pentachlorothiophenol ("PCTP") and a salt of PCTP. A preferred salt of PCTP is ZnPCTP. A suitable PCTP is sold by the Struktol Company (Stow, Ohio) under the tradename, A95. ZnPCTP is commercially available from EchinaChem (San Francisco, Calif.). These compounds also may function as cis-to-trans catalysts to convert some cis bonds in the polybutadiene to trans bonds. Antioxidants also may be added to the rubber compositions to prevent the breakdown of the elastomers. Other ingredients such as accelerators (for example, tetra methylthiuram), processing aids, dyes and pigments, wetting agents, surfactants, plasticizers, as well as other additives known in the art may be added to the rubber composition.

**[0043]** The core may be formed by mixing and forming the rubber composition using conventional techniques. These cores can be used to make finished golf balls by surrounding the core with outer core layer(s), intermediate layer(s), and/or cover materials as discussed further below. In another embodiment, the cores can be formed using highly neutralized polymer (HNP) compositions as disclosed in U.S. Pat. Nos. 6,756,436, 7,030,192, 7,402,629, and 7,517,289. The cores from the highly neutralized polymer compositions can be further cross-linked using any free-radical initiation sources including radiation sources such as gamma or electron beam as well as chemical sources such as peroxides and the like.

**[0044]** Golf balls made in accordance with this invention can be of any size, although the USGA requires that golf balls used in competition have a diameter of at least 1.68 inches and a weight of no greater than 1.62 ounces. For play outside of USGA competition, the golf balls can have smaller diameters and be heavier.

**[0045]** In some instances, a traditional thermoplastic or thermosetting composition may be used to make one layer and the vapor barrier layer may be used to make a different layer of the golf ball depending upon the desired ball construction playing performance properties. If a conventional thermoplastic or thermosetting composition is used in one layer (and the vapor barrier layer used in a different layer), then a wide variety of thermoplastic or thermosetting materials can be employed. These materials include for example, olefin-based copolymer ionomer resins (for example, Surlyn® ionomer resins and DuPont® HPF 1000 and HPF 2000, commercially available from E. I. du Pont de Nemours and Company; Iotek® ionomers, commercially available from ExxonMobil Chemical Company; Amplify® IO 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 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, for example, poly(meth)acrylic acid, which do not become part of an ionomeric copolymer; plastomers; flexomers; styrene/butadiene/sty-

rene block copolymers; styrene/ethylene-butylene/styrene block copolymers; dynamically vulcanized elastomers; copolymers of ethylene and vinyl acetates; copolymers of ethylene and methyl acrylates; polyvinyl chloride resins; polyamides, poly(amide-ester) elastomers, and graft copolymers of ionomer and polyamide including, for example, Pebax® thermoplastic polyether block amides, commercially available from Arkema Inc; cross-linked trans-polyisoprene 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.

**[0046]** While the inventive golf ball may be formed from a variety of differing and conventional materials for the intermediate layer(s), inner cover layer(s) and/or outer cover layer(s), preferred cover materials include, but are not limited to:

**[0047]** (1) Polyurethanes, such as those prepared from polyols and diisocyanates or polyisocyanates and/or their prepolymers;

**[0048]** (2) Polyureas; and

**[0049]** (3) Polyurethane-urea hybrids, blends or copolymers comprising urethane and urea segments.

**[0050]** Suitable polyurethane compositions comprise a reaction product of at least one polyisocyanate and at least one curing agent. The curing agent can include, for example, one or more polyamines, 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. Thus, the polyols described herein are suitable for use in one or both components of the polyurethane material, i.e., as part of a prepolymer and in the curing agent. Suitable polyurethanes are described in U.S. Patent Application Publication No. 2005/0176523, which is incorporated by reference in its entirety.

**[0051]** Any polyisocyanate available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyisocyanates include, but are not limited to, 4,4'-diphenylmethane diisocyanate (MDI); polymeric MDI; carbodiimide-modified liquid MDI; 4,4'-dicyclohexylmethane diisocyanate ( $H_{12}$ MDI); p-phenylene diisocyanate (PPDI); m-phenylene diisocyanate (MPDI); toluene diisocyanate (TDI); 3,3'-dimethyl-4,4'-biphenylene diisocyanate; isophoronediiisocyanate; 1,6-hexamethylene diisocyanate (HDI); naphthalene diisocyanate; xylene diisocyanate; p-tetramethylxylene diisocyanate; m-tetramethylxylene diisocyanate; ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; cyclohexyl diisocyanate; dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,4,4-trimethyl-1,6-hexane diisocyanate; tetracene diisocyanate; naphthalene diisocyanate; anthracene diisocyanate; isocyanurate of toluene diisocyanate; uretdione of hexamethylene diisocyanate; and mixtures thereof. Polyisocyanates are known to those of ordinary skill in the art as having more than one isocyanate group, e.g., di-isocyanate, tri-isocyanate, and tetra-isocyanate. Preferably, the polyisocyanate includes MDI, PPDI, TDI, or a mixture thereof, and more preferably, the polyisocyanate includes MDI. It should be understood that, as used herein, the term MDI includes 4,4'-diphenylmethane diisocyanate,

polymeric MDI, carbodiimide-modified liquid MDI, and mixtures thereof. Additionally, the prepolymers synthesized from these diisocyanates may be "low free monomer," understood by one of ordinary skill in the art to have lower levels of "free" isocyanate monomers, typically less than about 0.1% free isocyanate. Examples of "low free monomer" prepolymers include, but are not limited to Low Free Monomer MDI prepolymers, Low Free Monomer TDI prepolymers, and Low Free Monomer PPDI prepolymers.

**[0052]** Any polyol available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyols include, but are not limited to, polyether polyols, hydroxy-terminated polybutadiene (including partially/fully hydrogenated derivatives), polyester polyols, polycaprolactone polyols, and polycarbonate polyols. In one preferred embodiment, the polyol includes polyether polyol. Examples include, but are not limited to, polytetramethylene ether glycol (PTMEG), polyethylene propylene glycol, polyoxypropylene glycol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds and substituted or unsubstituted aromatic and cyclic groups. Preferably, the polyol of the present invention includes PTMEG.

**[0053]** In another embodiment, polyester polyols are included in the polyurethane material. Suitable polyester polyols include, but are not limited to, polyethylene adipate glycol; polybutylene adipate glycol; polyethylene propylene adipate glycol; o-phthalate-1,6-hexanediol; poly(hexamethylene adipate) glycol; and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

**[0054]** In another embodiment, polycaprolactone polyols are included in the materials of the invention. Suitable polycaprolactone polyols include, but are not limited to, 1,6-hexanediol-initiated polycaprolactone, diethylene glycol initiated polycaprolactone, trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

**[0055]** In yet another embodiment, polycarbonate polyols are included in the polyurethane material of the invention. Suitable polycarbonates include, but are not limited to, polyphthalate carbonate and poly(hexamethylene carbonate) glycol. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups. In one embodiment, the molecular weight of the polyol is from about 200 to about 4000.

**[0056]** Polyamine curatives are also suitable for use in the polyurethane composition of the invention and have been found to improve cut, shear, and impact resistance of the resultant balls. Preferred polyamine curatives include, but are not limited to, 3,5-dimethylthio-2,4-toluenediamine and isomers thereof; 3,5-diethyltoluene-2,4-diamine and isomers thereof, such as 3,5-diethyltoluene-2,6-diamine; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkyl-diamino diphenyl methane; p,p'-methylene dianiline; m-phenylenediamine; 4,4'-methylene-bis-(2-chloroaniline);

**[0057]** 4,4'-methylene-bis-(2,6-diethylaniline); 4,4'-methylene-bis-(2,3-dichloroaniline); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2', 3,3'-tetrachloro diamino

diphenylmethane; trimethylene glycol di-p-aminobenzoate; and mixtures thereof. Preferably, the curing agent of the present invention includes 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, such as ETHACURE® 300, commercially available from Albermarle Corporation of Baton Rouge, La. Suitable polyamine curatives, which include both primary and secondary amines, preferably have molecular weights ranging from about 64 to about 2000.

**[0058]** At least one of a diol, triol, tetraol, or hydroxy-terminated curatives may be added to the aforementioned polyurethane composition. Suitable diol, triol, and tetraol groups include ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy) benzene; 1,3-bis-[2-(2-hydroxyethoxy) ethoxy] benzene; 1,3-bis-{2-[2-(2-hydroxyethoxy) ethoxy] ethoxy} benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(β-hydroxyethyl) ether; hydroquinone-di-(β-hydroxyethyl) ether; and mixtures thereof. Preferred hydroxy-terminated curatives include 1,3-bis(2-hydroxyethoxy) benzene; 1,3-bis-[2-(2-hydroxyethoxy) ethoxy] benzene; 1,3-bis-{2-[2-(2-hydroxyethoxy) ethoxy] ethoxy} benzene; 1,4-butanediol, and mixtures thereof. Preferably, the hydroxy-terminated curatives have molecular weights ranging from about 48 to 2000. It should be understood that molecular weight, as used herein, is the absolute weight average molecular weight and would be understood as such by one of ordinary skill in the art.

**[0059]** Both the hydroxy-terminated and amine curatives can include one or more saturated, unsaturated, aromatic, and cyclic groups. Additionally, the hydroxy-terminated and amine curatives can include one or more halogen groups. The polyurethane composition can be formed with a blend or mixture of curing agents. If desired, however, the polyurethane composition may be formed with a single curing agent.

**[0060]** In a preferred embodiment of the present invention, saturated polyurethanes are used to form one or more of the cover layers, preferably the outer cover layer, and may be selected from among both castable thermoset and thermoplastic polyurethanes.

**[0061]** Thermosetting polyurethanes or polyureas are suitable for the outer cover layers of the golf balls of the invention.

**[0062]** Additionally, polyurethane can be replaced with or blended with a polyurea material. Polyureas are distinctly different from polyurethane compositions, giving better shear resistance. The polyurea-based compositions are preferably saturated in nature.

**[0063]** The polyether amine may be blended with additional polyols to formulate copolymers that are reacted with excess isocyanate to form the polyurea prepolymer. In one embodiment, less than about 30 percent polyol by weight of the copolymer is blended with the saturated polyether amine. In another embodiment, less than about 20 percent polyol by weight of the copolymer, preferably less than about 15 percent by weight of the copolymer, is blended with the polyether amine. The polyols listed above with respect to the polyurethane prepolymer, e.g., polyether polyols, polycaprolactone polyols, polyester polyols, polycarbonate polyols, hydrocarbon polyols, other polyols, and mixtures thereof, are also suitable for blending with the polyether amine. The molecular weight of these polymers may be from about 200 to about 4000, but also may be from about 1000 to about 3000, and more preferably are from about 1500 to about 2500.

**[0064]** The polyurea composition can be formed by crosslinking a polyurea prepolymer with a single curing agent or a blend of curing agents. The curing agent of the invention is preferably an amine-terminated curing agent, more preferably a secondary diamine curing agent so that the composition contains only urea linkages. In one embodiment, the amine-terminated curing agent may have a molecular weight of about 64 or greater. In another embodiment, the molecular weight of the amine-curing agent is about 2000 or less. As discussed above, certain amine-terminated curing agents may be modified with a compatible amine-terminated freezing point depressing agent or mixture of compatible freezing point depressing agents.

**[0065]** Suitable amine-terminated curing agents include, but are not limited to, ethylene diamine; hexamethylene diamine; 1-methyl-2,6-cyclohexyl diamine; tetrahydroxypropylene ethylene diamine; 2,2,4- and 2,4,4-trimethyl-1,6-hexanediamine; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,4-bis-(sec-butylamino)-cyclohexane; 1,2-bis-(sec-butylamino)-cyclohexane; derivatives of 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 4,4'-dicyclohexylmethane diamine; 1,4-cyclohexane-bis-(methylamine); 1,3-cyclohexane-bis-(methylamine); diethylene glycol di-(aminopropyl) ether; 2-methylpentamethylene-diamine; diaminocyclohexane; diethylene triamine; triethylene tetramine; tetraethylene pentamine; propylene diamine; 1,3-diaminopropane; dimethylamino propylamine; diethylamino propylamine; dipropylene triamine; imido-bis-propylamine; monoethanolamine, diethanolamine; 3,5-diethyltoluene-2,4-diamine;

**[0066]** triethanolamine; monoisopropanolamine, diisopropanolamine; isophoronediamine; 4,4'-methylenebis-(2-chloroaniline); 3,5-dimethylthio-2,4-toluenediamine; 3,5-dimethylthio-2,6-toluenediamine; 3,5-diethylthio-2,4-toluenediamine; 3,5-diethylthio-2,6-toluenediamine; 4,4'-bis-(sec-butylamino)-diphenylmethane and derivatives thereof; 1,4-bis-(sec-butylamino)-benzene; 1,2-bis-(sec-butylamino)-benzene; N,N'-dialkylamino-diphenylmethane; N,N,N',N'-tetrakis (2-hydroxypropyl) ethylene diamine; trimethyleneglycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate; 4,4'-methylenebis-(3-chloro-2,6-diethylaniline); 4,4'-methylenebis-(2,6-diethylaniline); meta-phenylenediamine; paraphenylenediamine; and mixtures thereof. In one embodiment, the amine-terminated curing agent is 4,4'-bis-(sec-butylamino)-dicyclohexylmethane.

**[0067]** Suitable saturated amine-terminated curing agents include, but are not limited to, ethylene diamine; hexamethylene diamine; 1-methyl-2,6-cyclohexyl diamine; tetrahydroxypropylene ethylene diamine; 2,2,4- and 2,4,4-trimethyl-1,6-hexanediamine; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,4-bis-(sec-butylamino)-cyclohexane; 1,2-bis-(sec-butylamino)-cyclohexane; derivatives of 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; ; 4,4'-dicyclohexylmethane diamine; 4,4'-methylenebis-(2,6-diethylaminocyclohexane); 1,4-cyclohexane-bis-(methylamine); 1,3-cyclohexane-bis-(methylamine); diethylene glycol di-(aminopropyl) ether; 2-methylpentamethylene-diamine; diaminocyclohexane; diethylene triamine; triethylene tetramine; tetraethylene pentamine; propylene diamine; 1,3-diaminopropane; dimethylamino propylamine; diethylamino propylamine; imido-bis-propylamine; monoethanolamine, diethanolamine; triethanolamine; monoisopropanolamine, diisopropanolamine; isophoronediamine; triiso-

propanolamine; and mixtures thereof. In addition, any of the polyether amines listed above may be used as curing agents to react with the polyurea prepolymers.

**[0068]** Alternatively, other suitable polymers include partially or fully neutralized ionomer, metallocene, or other single-site catalyzed polymer, polyester, polyamide, non-ionomeric thermoplastic elastomer, copolyether-esters, copolyether-amides, polycarbonate, polybutadiene, polyisoprene, polystyrene block copolymers (such as styrene-butadiene-styrene), styrene-ethylene-propylene-styrene, styrene-ethylene-butylene-styrene, and the like, and blends thereof.

**[0069]** Cover layers of the inventive golf ball may also be formed from ionomeric polymers, preferably highly-neutralized ionomers (HNP). In a preferred embodiment, at least one intermediate layer of the golf ball is formed from an HNP material or a blend of HNP materials. The acid moieties of the HNP's, 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 HNP's can be also be blended with a second polymer component, which, if containing an acid group, may be neutralized in a conventional manner, by organic fatty acids, or both. The second polymer component, which may be partially or fully neutralized, preferably comprises ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, polyamides, polycarbonates, polyesters, polyurethanes, 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, and a flexural modulus of between about 3,000 psi and about 200,000 psi.

**[0070]** In one embodiment of the present invention the HNP's are ionomers and/or their acid precursors that are preferably neutralized, either fully or partially, with organic acid copolymers or the salts thereof. The acid copolymers are preferably  $\alpha$ -olefin, such as ethylene,  $C_{3-8}$   $\mu,\beta$ -ethylenically unsaturated carboxylic acid, such as acrylic and methacrylic acid, copolymers. They may optionally contain a softening monomer, such as alkyl acrylate and alkyl methacrylate, wherein the alkyl groups have from 1 to 8 carbon atoms.

**[0071]** The acid copolymers can be described as E/X/Y copolymers where E is ethylene, X is an  $\alpha,\beta$ -ethylenically unsaturated carboxylic acid, and Y is a softening comonomer. In a preferred embodiment, X is acrylic or methacrylic acid and Y is a  $C_{1-8}$  alkyl acrylate or methacrylate ester. X is preferably present in an amount from about 1 to about 35 weight percent of the polymer, more preferably from about 5 to about 30 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer. Y is preferably present in an amount from about 0 to about 50 weight percent of the polymer, more preferably from about 5 to about 25 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer.

**[0072]** Specific acid-containing ethylene copolymers include, but are not limited to, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/n-butyl acrylate, ethylene/methacrylic acid/iso-butyl acrylate, ethylene/acrylic acid/iso-butyl acrylate, ethylene/methacrylic acid/n-butyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacry-

late. Preferred acid-containing ethylene copolymers include, ethylene/methacrylic acid/n-butyl acrylate, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/acrylic acid/ethyl acrylate, ethylene/methacrylic acid/ethyl acrylate, and ethylene/acrylic acid/methyl acrylate copolymers. The most preferred acid-containing ethylene copolymers are, ethylene/(meth) acrylic acid/n-butyl, acrylate, ethylene/(meth) acrylic acid/ethyl acrylate, and ethylene/(meth) acrylic acid/methyl acrylate copolymers.

**[0073]** Ionomers are typically neutralized with a metal cation, such as Li, Na, Mg, K, Ca, or Zn. It has been found that by adding sufficient organic acid or salt of organic acid, along with a suitable base, to the acid copolymer or ionomer, the ionomer can be neutralized, without losing processability, to a level much greater than for a metal cation. Preferably, the acid moieties are neutralized greater than about 80%, preferably from 90-100%, most preferably 100% without losing processability. This is accomplished by melt-blending an ethylene  $\alpha,\beta$ -ethylenically unsaturated carboxylic acid copolymer, for example, with an organic acid or a salt of organic acid, and adding a sufficient amount of a cation source to increase the level of neutralization of all the acid moieties (including those in the acid copolymer and in the organic acid) to greater than 90%, (preferably greater than 100%).

**[0074]** The organic acids of the present invention are aliphatic, mono- or multi-functional (saturated, unsaturated, or multi-unsaturated) organic acids. Salts of these organic acids may also be employed. The salts of organic acids of the present invention 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).

**[0075]** The ionomers of the invention may also be more conventional ionomers, i.e., partially-neutralized with metal cations. The acid moiety in the acid copolymer is neutralized about 1 to about 90%, preferably at least about 20 to about 75%, and more preferably at least about 40 to about 70%, to form an ionomer, by a cation such as lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, aluminum, or a mixture thereof.

**[0076]** The moisture vapor barrier layer(s) of the inventive golf ball may also contain additives, ingredients, and other materials in amounts that do not detract from the properties of the final composition. These additive materials include, but are not limited to, activators such as calcium or magnesium oxide; fatty acids such as stearic acid and salts thereof; fillers and reinforcing agents such as organic or inorganic particles, for example, clays, talc, calcium, magnesium carbonate, silica, aluminum silicates, zeolites, powdered metals, and organic or inorganic fibers, plasticizers such as dialkyl esters of dicarboxylic acids; surfactants; softeners; tackifiers; waxes; ultraviolet (UV) light absorbers and stabilizers; anti-oxidants; optical brighteners; whitening agents such as titanium dioxide and zinc oxide; dyes and pigments; processing aids; release agents; and wetting agents. These compositions provide improved melt processability, and a balance of ball performance.



**[0077]** Blowing/foaming agents may also be particularly compatible with the moisture vapor barrier layer incorporated golf ball of the invention, including, for example those disclosed in U.S. Pat. No. 7,708,654. Typical physical foaming/blowing agents include volatile liquids such as freons (CFCs), other halogenated hydrocarbons, water, aliphatic hydrocarbons, gases, and solid blowing agents, i.e., compounds that liberate gas as a result of desorption of gas. Preferably, the blowing agent includes an adsorbent. Typical adsorbents include, for example, activated carbon, calcium carbonate, diatomaceous earth, and silicates saturated with carbon dioxide.

**[0078]** Chemical foaming/blowing agents are more preferred, particularly when the core includes thermoplastics such as ionomers, highly neutralized polymers, and polyolefins. Chemical blowing agents may be inorganic, such as ammonium carbonate and carbonates of alkali metals, or may be organic, such as azo and diazo compounds, such as nitrogen-based azo compounds. Suitable azo compounds include, but are not limited to, 2,2'-azobis(2-cyanobutane), 2,2'-azobis(methylbutyronitrile), azodicarbonamide, p,p'-oxybis(benzene sulfonyl hydrazide), p-toluene sulfonyl semicarbazide, p-toluene sulfonyl hydrazide. Other blowing agents include any of the Celogens, sold by Crompton Chemical Corporation, and nitroso compounds, sulfonylhydrazides, azides of organic acids and their analogs, triazines, tri- and tetrazole derivatives, sulfonyl semicarbazides, urea derivatives, guanidine derivatives, and esters such as alkoxyboroxines. Other possible blowing agents include agents that liberate gasses as a result of chemical interaction between components such as mixtures of acids and metals, mixtures of organic acids and inorganic carbonates, mixtures of nitriles and ammonium salts, and the hydrolytic decomposition of urea.

**[0079]** Alternatively, low specific gravity can be achieved by incorporating low density fillers or agents such as hollow fillers or microspheres in the polymeric matrix, where the cured composition has the preferred specific gravity. Moreover, the polymeric matrix can be foamed to decrease its specific gravity, microballoons, or other low density fillers as described in U.S. Pat. No. 6,692,380 ("380 Patent"). The '380 patent is incorporated by reference in its entirety.

**[0080]** The moisture barrier composition in the golf ball of this invention may be blended with non-ionomeric and olefin-based ionomeric polymers to form the composition that will be used to make the golf ball layer. Examples of non-ionomeric polymers include vinyl resins, polyolefins including those produced using a single-site catalyst or a metallocene catalyst, polyurethanes, polyureas, polyamides, polyphenylenes, polycarbonates, polyesters, polyacrylates, engineering thermoplastics, and the like. Also, in one embodiment of the invention, processability of the golf ball of the invention may even be enhanced by incorporating in the core a metallocene-catalyzed polybutadiene.

**[0081]** Olefin-based ionomers, such as ethylene-based copolymers, normally include an 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. "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 ionic 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. Or, the neutralization level may be from about 80 to 100%, more preferably 90 to 100%, and most preferably 95 to 100%. The blend may contain about 5 to about 30% by weight of the moisture barrier composition and about 95 to about 70% by weight of a partially, highly, or fully-neutralized olefin-based ionomeric copolymer. The above-mentioned blends may contain one or more suitable compatibilizers such as glycidyl acrylate or glycidyl methacrylate or maleic anhydride containing-polymers.

**[0082]** The core may contain sections having the same hardness or different hardness levels. That is, there can be uniform hardness throughout the different sections of the core or there can be hardness gradients across the layers. For example, in single cores, there may be a hard-to-soft gradient (a "positive" gradient) from the surface of the core to the geometric center of the core. In other instances, there may be a soft-to-hard gradient (a "negative" gradient) or zero hardness gradient from the core's surface to the core's center. For dual core golf balls, the inner core layer may have a surface hardness that is less than the geometric center hardness to define a first "negative" gradient. As discussed above, an outer core layer may be formed around the inner core layer, and the outer core layer may have an outer surface hardness less than its inner surface hardness to define a second "negative" gradient. In other versions, the hardness gradients from surface to center may be hard-to-soft ("positive"), or soft-to-hard ("negative"), or a combination of both gradients. In still other versions the hardness gradients from surface to center may be "zero" (that is, the hardness values are substantially the same.) Methods for making cores having positive, negative, and zero hardness gradients are known in the art as described in, for example, U.S. Pat. Nos. 7,537,530; 7,537,529; 7,427,242; and 7,410,429, the disclosures of which are hereby incorporated by reference.

**[0083]** A golf ball according to the invention may therefore incorporate the moisture vapor barrier composition in a core to achieve various hardness gradients therein. For example, the moisture vapor barrier composition may be incorporated in a single-core constituting a solid core having a "positive" hardness gradient (that is, the outer surface of the core is harder than its geometric center.) In a second embodiment, the moisture vapor barrier composition may be incorporated in a dual-core comprising an inner core and a surrounding outer 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 zero. The terms, zero hardness gradient and negative hardness gradient, may be used herein interchangeably to refer to hardness gradients of negative 1 to negative 25. The term, “positive hardness gradient” as used herein, means a surface to center Shore C hardness gradient of 8 or greater, preferably 10 or greater, and most preferably 20 or greater. 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 moisture vapor barrier composition containing core may have a step 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.

**[0084]** 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 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.

**[0085]** The outer surface hardness of a golf ball layer is measured on the actual outer surface of the layer and 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 indenter 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 conform to ASTM D-2240. 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.

**[0086]** 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.

**[0087]** 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 mate-

rial 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 was measured according to the test methods D-2240.

**[0088]** 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. See, e.g., *Compression by Any Other Name*,

**[0089]** Science and Golf IV, Proceedings of the World Scientific Congress of Golf (Eric Thain ed., Routledge, 2002) (“J. Dalton”) The term compression, as used herein, refers to Atti or PGA compression and is measured using an Atti compression test device. A piston compresses a ball against a spring and the piston remains fixed while deflection of the spring is measured at 1.25 mm (0.05 inches). Where a core has a very low stiffness, the compression measurement will be zero at 1.25 mm. In order to measure the compression of a core using an Atti compression tester, the core must be shimmed to a diameter of 1.680 inches because these testers are designed to measure objects having that diameter. Atti compression units can be converted to Riehle (cores), Riehle (balls), 100 kg deflection, 130-10 kg deflection or effective modulus using the formulas set forth in J.

**[0090]** Dalton. The approximate relationship that exists between Atti or PGA compression and Riehle compression can be expressed as: (Atti or PGA compression)=(160-Riehle Compression). Thus, a Riehle compression of 100 would be the same as an Atti compression of 60.

**[0091]** COR, as used herein, is determined by firing a golf ball or golf ball subassembly (e.g., a golf ball core) from an air cannon at two given velocities and calculating the COR at a velocity of 125 ft/s. Ball velocity is calculated as a ball approaches ballistic light screens which are located between the air cannon and a steel plate at a fixed distance. As the ball travels toward the steel plate, each light screen is activated, and the time at each light screen is measured. This provides an incoming transit time period inversely proportional to the ball's incoming velocity. The ball impacts the steel plate and rebounds through the light screens, which again measure the time period required to transit between the light screens. This provides an outgoing transit time period inversely proportional to the ball's outgoing velocity. COR is then calculated as the ratio of the outgoing transit time period to the incoming transit time period,  $COR = V_{out}/V_{in} = T_{in}/T_{out}$ . Preferably, a golf ball according to the present invention has a COR of at least about 0.78, more preferably, at least about 0.80.

**[0092]** The spin rate of a golf ball also remains an important golf ball characteristic. High spin rate allows skilled players more flexibility in stopping the ball on the green if they are able to control a high spin ball. On the other hand, recreational players often prefer a low spin ball since they do not have the ability to intentionally control the ball, and lower spin balls tend to drift less off the green.

**[0093]** Golf ball spin is dependent on variables including, for example, distribution of the density or specific gravity within a golf ball. For example, when the center has a higher density or specific gravity than the outer layers, a lower moment of inertia results which increases spin rate. Alternatively, when the density or specific gravity is concentrated in the outer regions of the golf ball, a higher moment of inertia results with a lower spin rate. The moment of inertia for a golf ball of the invention may be from about 0.410 oz-in<sup>2</sup> to about

0.470 oz-in<sup>2</sup>. The moment of inertia for a one piece ball that is 1.62 ounces and 1.68 inches in diameter may be approximately 0.4572 oz-in<sup>2</sup>, which is the baseline moment of inertia value.

**[0094]** Accordingly, by varying the materials and the hardness of the regions of each core layer, different moments of inertia may be achieved for the golf ball of the present invention. In one embodiment, the resulting golf ball has a moment of inertia of from about 0.440 to about 0.455 oz-in<sup>2</sup>. In another embodiment, the golf balls of the present invention have a moment of inertia of from about 0.456 oz-in<sup>2</sup> to about 0.470 oz-in<sup>2</sup>. In yet another embodiment, the golf ball has a moment of inertia of from about 0.450 oz-in<sup>2</sup> to about 0.460 oz-in<sup>2</sup>.

**[0095]** Unless otherwise expressly specified, all of the numerical ranges, amounts, values and percentages such as those for amounts of materials, and others in the specification may be read as if prefaced by the word “about” even though the term “about” may not expressly appear with the value, amount or range. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

**[0096]** Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. Furthermore, when numerical ranges of varying scope are set forth herein, it is contemplated that any combination of these values inclusive of the recited values may be used.

**[0097]** While it is apparent that the illustrative embodiments of the invention disclosed herein fulfill the preferred embodiments of the present invention, it is appreciated that numerous modifications and other embodiments may be devised by those skilled in the art. Examples of such modifications include reasonable variations of the numerical values and/or materials and/or components discussed above. Hence, the numerical values stated above and claimed below specifically include those values and the values that are approximate to those stated and claimed values. Therefore, it will be understood that the appended claims are intended to cover all such modifications and embodiments, which would come within the spirit and scope of the present invention.

**[0098]** The invention described and claimed herein is not to be limited in scope by the specific embodiments herein disclosed, since these embodiments are intended as illustrations of several aspects of the invention. Any equivalent embodiments are intended to be within the scope of this invention. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. For example, the compositions of the present invention may be used in a variety of equipment. Such modifications are also intended to fall within the scope of the appended claims.

**[0099]** While any of the embodiments herein may have any known dimple number and pattern, a preferred number of

dimples is 252 to 456, and more preferably is 328 to 392. The dimples may comprise any width, depth, and edge angle disclosed in the prior art and the patterns may comprises multitudes of dimples having different widths, depths and edge angles. The parting line configuration of said pattern may be either a straight line or a staggered wave parting line (SWPL). In one embodiment, the golf ball has 328, 330, 332, or 392 dimples, comprises 5 to 7 dimples sizes, and the parting line is a SWPL.

**[0100]** In any of these embodiments the single-layer core may be replaced with a two or more layer core wherein at least one core layer has a negative hardness gradient. Other than in the operating examples, or unless otherwise expressly specified, all of the numerical ranges, amounts, values and percentages such as those for amounts of materials and others in the specification may be read as if prefaced by the word “about” even though the term “about” may not expressly appear with the value, amount or range.

**[0101]** Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

What is claimed is:

1. A golf ball comprising:  
a core, a cover and optionally an intermediate layer disposed between the core and the cover,  
wherein at least one of the core, the intermediate layer and the cover comprises a moisture vapor barrier layer formed from a moisture vapor barrier composition comprising at least one diene rubber and at least one fluorinated silane treated filler.
2. The golf ball of claim 1, wherein the filler is selected from the group comprising silica, carbon black, graphite, nano graphite, carbon nanotubes and carbon nanoflakes.
3. The golf ball of claim 2, wherein the silica is precipitated silica.
4. The golf ball of claim 2, wherein the filler further comprises at least one of a non-fluorinated silane treated silica, fibers, flakes, and a sulfur-comprising organosilicon composition.
5. The golf ball of claim 1, wherein the filler is present in an amount of from about 1 phr to about 40 phr.
6. The golf ball of claim 1, wherein the diene rubber comprises high cis polybutadiene rubber that is cobalt-catalyzed, nickel-catalyzed, lithium-catalyzed, or neodymium-catalyzed.
7. The golf ball of claim 1, wherein the diene rubber comprises ethylene propylene diene monomer rubber.
8. The golf ball of claim 1, wherein the diene rubber comprises a blend of high cis polybutadiene rubber and at least one different rubber selected from the group comprising natu-

ral rubber, balata, trans polyisoprene, styrene butadiene rubber, ethylene propylene rubber, ethylene propylene diene monomer rubber, butyl rubber, halo-butyl rubber, low-cis polybutadiene rubber, and trans polybutadiene rubber.

9. The golf ball of claim 8, wherein the ratio of high cis polybutadiene rubber to the at least one different rubber is from about 9:1 to about 1:9.

10. The golf ball of claim 8, wherein the ratio of high cis polybutadiene rubber to the at least one different rubber is from about 6:4 to about 4:6.

11. The golf ball of claim 1, wherein the vapor barrier composition has a moisture vapor transmission rate of about 1.5 grams-mm/m<sup>2</sup>-day or less.

12. A golf ball comprising:

a core, a cover and a moisture barrier layer disposed between the core and the cover,

wherein the moisture vapor barrier layer has a moisture vapor transmission rate that is lower than that of the cover and the moisture vapor barrier layer is formed from a vapor barrier composition comprising at least one diene rubber and at least one fluorinated silane treated filler.

13. A golf ball comprising:

a core comprising an untreated region and a treated outer surface, the treated outer surface having a first moisture vapor transmission rate and the untreated region having a second moisture vapor transmission rate, the treated outer surface being treated with and comprising a moisture vapor barrier composition formed from at least one diene rubber and at least one fluorinated silane treated filler such that the first moisture vapor transmission rate is lower than the second moisture vapor transmission rate.

14. A golf ball comprising:

a core and a cover disposed about the core,  
wherein the core comprises an inner core layer and an outer core layer, said inner core layer having a moisture vapor transmission rate X and the outer core layer having a moisture vapor transmission rate Y, the outer core layer comprising a moisture vapor barrier composition formed from at least one diene rubber and at least one fluorinated silane treated filler such that  $X > Y$ .

15. The golf ball of claim 14, wherein  $Y \leq 0.5X$ .

16. The golf ball of claim 14, wherein  $Y \leq 0.3X$ .

17. The golf ball of claim 14, wherein  $Y \leq 0.15X$ .

18. A golf ball comprising an untreated region and a treated outer surface, the treated outer surface having a moisture vapor transmission rate X and the untreated region having a moisture vapor transmission rate Y, the treated outer surface being treated with and comprising a moisture vapor barrier composition formed from at least one diene rubber and at least one fluorinated silane treated filler such that  $X < Y$ .

19. The golf ball of claim 18, wherein  $X \leq 0.5Y$ .

20. The golf ball of claim 18, wherein  $X \leq 0.25Y$ .

21. The golf ball of claim 18, wherein  $X \leq 0.10Y$ .

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