MULTI-LAYERED CORES HAVING SELECTIVE WEIGHT DISTRIBUTION FOR GOLF BALLS

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ABSTRACT

Multi-piece golf balls containing a multi-layered core or a dual-core are provided. The cores have selective weighting configurations (SWC). Particularly, the core layers are made of different compositions having different specific gravity levels or densities. Preferably, rubber and high neutralized ethylene acid copolymer compositions are used to form at least one layer in the core. The rubber and ionomer compositions may be loaded with fillers to adjust the specific gravity levels. The moment of inertia of the ball is adjusted and the resulting ball has good resiliency and spin control properties.
MULTI-LAYERED CORES HAVING SELECTIVE WEIGHT DISTRIBUTION FOR GOLF BALLS

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

The present invention generally relates to multi-piece golf balls having a solid core of at least two layers and cover of at least one layer. Preferably, the ball contains a multi-layered core having an inner core, intermediate core layer, and outer core layer, or a dual-core having an inner core and surrounding outer core layer. The cores have selective weighting configurations (SWC), whereby the core layers have different densities. The cores are used to provide finished balls having high resiliency and spin-control properties.

[0002] 2. Brief Review of the Related Art

Multi-piece, solid golf balls having a solid inner core protected by a cover are used today by recreational and professional golfers. The golf balls may have single-layered or multi-layered cores. Normally, the core layers are made of a highly resilient natural or synthetic rubber material such as, for example, styrene butadiene, polybutadiene, poly(iso-prene), or poly(trans-isoprene) or highly neutralized ethylene acid copolymers (HNPs). The covers may be single or multi-layered and made of a durable material such as, for example, HNPs, polyamides, polyesters, polyurethanes, or polyureas. Manufacturers of golf balls use different constructions (for example, three-piece, four-piece, and five-piece balls) to impart specific properties and features.

[0003] The core is the primary source of resiliency for the golf ball and is often referred to as the “engine” of the ball. The resiliency or coefficient of restitution (“COR”) of a golf ball (or golf ball component such as a core) means the ratio of a ball’s rebound velocity to its initial incoming velocity when the ball is fired out of an air cannon into a rigid plate. The COR for a golf ball is written as a decimal value between zero and one. A golf ball may have different COR values at different initial velocities. The United States Golf Association (USGA) sets limits on the initial velocity of the ball so one objective of golf ball manufacturers is to maximize the COR under these conditions. Balls (or cores) 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. In general, the COR of the ball will increase as the hardness of the ball is increased. The test methods for measuring the COR are described in further detail below. In some conventional golf balls, materials are used to increase the hardness of the core so the resiliency of the core is increased, and this, in turn, causes the compression of the core to increase.

[0004] In general, compression refers to the deflection that a golf ball (or golf ball component such as a core) undergoes when subjected to a compressive load. Several different methods may be used to measure compression of the golf ball and its components. The compression is commonly measured using Atti or Richile compression gauges. In the Atti method, as described further below, a piston is used to compress a ball against a spring. The travel distance and load of the piston are fixed and the deflection of the spring is measured. If the core is relatively soft, the spring will deflect only by a minimal amount. On the other hand, if the core is relatively hard, the spring will deflect a significant amount. The test methods for measuring compression are described in further detail below.

[0005] Cores having a higher compression are harder and tend to have good durability and resiliency. Players may achieve greater flight distance when using such golf balls, which is particularly desirable when hitting the ball off the tee. However, some high compression balls are relatively stiff and this may have a detrimental effect. For example, such balls tend to have a low initial spin rate and this makes the ball more difficult to control. This can be particularly troubling when making approach shots near the green. On the other hand, they have a higher spin rate, flight distance may be sacrificed. Some players may have a more difficult time driving such balls a long distance off the tee.

[0006] Golf ball manufacturers have looked at adjusting the density or specific gravity among the multiple layers of the golf ball to control its spin rate. General, the total weight of a golf ball has to conform to weight limits set by the United States Golf Association (“USGA”). Although the total weight of the golf ball is controlled, the distribution of weight within the ball can vary. Redistributing the weight or mass of the golf ball either toward the center of the ball or toward the outer surface of the ball changes its flight and spin properties.

[0007] For example, the weight can be shifted towards the center of the ball to increase the spin rate as described in Yamada, U.S. Pat. No. 4,625,964, wherein the golf ball contains a core, an intermediate layer, and a cover, and the core has a specific gravity of at least 1.50 and a diameter of less than 32 mm, the intermediate layer having a lower specific gravity than the core. Chikarashi et al., U.S. Pat. No. 5,048,838 discloses another three-piece golf ball containing a two-piece solid core and a cover. The dense inner core has a diameter in the range of 15-25 mm with a specific gravity of 1.2 to 4.0 and the outer core layer has a specific gravity of 0.1 to 3.0 less than the specific gravity of the inner core. Gentiluomo, U.S. Pat. No. 5,104,126 discloses a ball with a dense inner core made of steel, lead, brass, zinc, copper, and a filled elastomer, wherein the core has a specific gravity of at least 1.25. The inner core is encapsulated by a lower density syntactic foam composition and this construction is encapsulated by an ionomer cover. Yabuki et al., U.S. Pat. No. 5,482,285 describes a three-piece golf ball having an inner core and outer core encapsulated by an ionomer cover. The specific gravity of the outer core is reduced so that it falls within the range of 0.2 to 1.0. The specific gravity of the inner core is adjusted so that the total weight of the inner/outer core falls within a range of 32.0 to 39.0 g. In other instances, the weight can be shifted to the outside portion of the ball and away from the center. For example, Sullivan and Nesbitt, U.S. Pat. No. 6,120,393 discloses golf balls having a low spin rate. The balls comprise a relatively soft, multi-piece core and a hard cover. The inner core is hollow and may be filled with gases, while the outer core layer is made of a soft, resilient material. Sullivan and Nesbitt, U.S. Pat. No. 6,142,887 disclose a golf ball containing a core, a thin spherical layer, and a polymeric outer cover. The thin spherical layer comprises a metal, ceramic, or composite material such as silicon carbide, glass, carbon, boron carbide, and aramid materials.

[0010] Although some conventional multi-layered core constructions are generally effective in providing high resiliency golf balls, there is a continuing need for improved core constructions in golf balls. Particularly, it would be desirable to have multi-layered core constructions that would have selective weighting configurations (SWC) to provide the ball with good flight distance along with spin control. The present
invention provides core constructions and golf balls having such properties as well as other advantageous features, and benefits.

SUMMARY OF THE INVENTION

[0011] The present invention provides a multi-piece golf ball comprising a solid core having at least one layer and a cover having at least one layer. The golf ball may have different constructions. For instance, in one version, a golf ball having a three-layered ("multi-layer") core is made; while in another version, a golf ball having a two-layered ("dual") core is made. As discussed further below, in the balls of this invention, the overall density of the core is generally balanced. Some bits of mass are positioned relatively close to the center of the ball, while other bits of mass are positioned away from the center of the ball. Thus, the ball does not have a relatively high or low moment of inertia. Rather, the ball can be described as having a relative "medium moment of inertia." Thus, the ball has generally good flight distance and spin control.

[0012] In a first preferred embodiment, the golf ball comprises a multi-layer core having an inner core, intermediate core layer, and outer core layer; along with a cover disposed about the core. The inner core preferably has a diameter in the range of about 0.015 to about 0.900 inches and specific gravity in the range of about 1.18 to about 5.00 g/cc. The intermediate core layer preferably has a thickness in the range of about 0.100 to about 0.600 inches and specific gravity in the range of about 0.800 to about 1.20 g/cc. The outer core layer preferably has a thickness in the range of about 0.100 to about 0.200 inches and specific gravity of about 1.20 to about 5.00 g/cc. Preferably, the specific gravity of the inner core (SG_{inner}) is greater than the specific gravity of the intermediate core (SG_{intermediate}) and the SG_{intermediate} is less than the specific gravity of the outer core (SG_{outer}).

[0013] In one version, at least one of the core layers is formed of a rubber material, such as, for example, polybutadiene, ethylene-propylene rubber, ethylene-propylene-diene rubber, polyisoprene, styrene-butadiene rubber, polyalk-enamers, butyl, butylrubber, or polyolefin elastomers. And, at least one of the core layers is formed from a ionomer composition comprising an ethylene acid copolymer containing acid groups such that greater than 70% of the acid groups are neutralized. More particularly, a multi-layered core comprising an inner core formed of a rubber composition; an intermediate core formed of the highly neutralized ionomer composition; and outer core layer formed of a rubber composition may be prepared. The rubber and ionomer compositions may contain specific gravity fillers to adjust the density of the respective layers. For example, these fillers may be selected from the group consisting of metal powder, metal alloy powder, metal oxide, metal stearates, particulates, carbonaceous material, and mixtures thereof.

[0014] In a second preferred embodiment, the golf ball comprises a dual-core having an inner core and outer core layer; along with a cover disposed about the core. The inner core preferably has a diameter in the range of about 0.015 to about 0.900 inches and specific gravity in the range of about 1.18 to about 5.00 g/cc. The outer core layer preferably has a thickness in the range of about 0.100 to about 0.600 inches and specific gravity in the range of about 0.100 to about 0.200 inches so that the specific gravity of the inner core (SG_{inner}) is greater than the specific gravity of the outer core (SG_{outer}).

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] 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:

[0016] FIG. 1 is a cross-sectional view of a four-piece golf ball having a multi-layered core made in accordance with the present invention; and

[0017] FIG. 2 is a cross-sectional view of a three-piece golf ball having a dual-core made in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0018] Golf Ball Constructions

[0019] 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 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 having a dual-core and a cover is made. The dual-core includes an inner core (center) and surrounding outer core layer. In another version, a four-piece golf ball comprising a dual-core and dual-cover comprising an inner cover and outer cover is made. In yet another construction, a four-piece or five-piece golf ball having a multi-layered core comprising an inner core (center), intermediate core layer, and outer core layer, may be made. The golf balls of this invention may further contain an intermediate layer(s). As used herein, the term, "intermediate layer" means a layer of the ball disposed between the core and cover. The intermediate layer also may be referred to as a casing or mantle layer. 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.

[0020] Referring to FIG. 1, one version of a golf ball that can be made in accordance with this invention is generally indicated at (12). The ball (12) contains a multi-layered core (14) having an inner core (center) (14a); intermediate core layer (14b); and outer core layer (14c) surrounded by a single-layered cover (16). The inner core (14a) is relatively small in volume and generally has a diameter within a range having a lower limit of about 0.15 or 0.25 or 0.35 or 0.45 or 0.55 inches and an upper limit of about 0.65 or 0.75 or 0.80 or 0.90 or 0.95 inches. In one preferred version, the inner core has a diameter in the range of about 0.15 to about 0.50 inches, preferably about 0.20 to about 0.50 inches. In the other hand, the intermediate layer (14b) is relatively large in volume and generally has a thickness in the range having a lower limit of about 0.10 or 0.20 or 0.30 or 0.40 or 0.50 or 0.60 inches. In one preferred version, the intermediate core layer (14b) has a thickness in the range of about 0.65 or 0.60 or 0.50 inches, more preferably about 0.25 to about 0.50 inches. In one preferred version, the outer core layer (14c) generally has a thickness within a range having a lower limit of about 0.01 or 0.02 or 0.025 or 0.05 or 0.10 or 0.15 inches and an upper limit of about 0.070 or 0.080 or 0.10 or 0.20 inches. In one preferred version, the outer core layer has a thickness in the range of about 0.03 to about 0.15 inches, more preferably about 0.20 to about 0.25 inches.
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. For play outside of United States Golf Association (USGA) rules, the golf balls can be of a smaller size. Normally, golf balls are manufactured in accordance with USGA requirements and have a diameter in the range of about 1.68 to about 1.80 inches. In general, the multi-layered core (14) has an overall diameter ranging from having a lower limit of about 1.00 or 1.20 or 1.30 or 1.40 inches and an upper limit of about 1.58 or 1.60 or 1.62 or 1.64 inches. Referring to Fig. 2, in another version, the golf ball (18) contains a dual-core (20) having an inner core (center) (20a) and outer core layer (20b), and there is no intermediate core layer present. The dual-core is surrounded by a single-layered cover (22).

In the multi-layered core version, as shown in Fig. 1, the inner core (14a) preferably has a relatively high specific gravity. In general, the inner core (14a) has a specific gravity within a range having a lower limit of about 1.18 or 1.50 or 2.00 or 2.50 g/cc and an upper limit of about 3.00 or 3.50 or 4.00 or 4.50 or 5.00 g/cc. In a preferred embodiment, the inner core has a specific gravity of about 1.20 to about 3.50 g/cc, more preferably about 1.25 to about 3.00 g/cc. Meanwhile, the intermediate core layer (14b) preferably has a relatively low specific gravity. The intermediate core (14b) generally has a specific gravity within a range having a lower limit of about 0.080 or 0.100 or 0.400 or 0.600 or 0.800 g/cc and an upper limit of about 1.00 or 1.10 or 1.20 g/cc. In a preferred embodiment, the intermediate core layer has a specific gravity of about 0.90 to about 1.18 g/cc, more preferably about 0.905 to about 1.15 g/cc. In a manner similar to the inner core, the outer core (14c) has a specific gravity within a range having a lower limit of about 1.18 or 1.50 or 2.00 or 2.50 g/cc and an upper limit of about 3.00 or 3.50 or 4.00 or 4.50 or 5.00 g/cc. In a particularly preferred embodiment, the specific gravities of the center and outer core layer are equal or substantially the same. For purposes of the present invention, specific gravities are substantially the same if they are the same or within 0.1 g/cc of each other. In the dual-layer core version, as shown in Fig. 2, the inner core (20a) preferably has a specific gravity within a range of about 1.18 to about 5.00 g/cc; and the outer core layer (20b) has a specific gravity within a range of about 0.80 to about 1.20 g/cc.

Preferably, the specific gravity of the inner core (SGinner) is greater than the specific gravity of the intermediate core layer (SGintermediate). And, the specific gravity of the intermediate core layer (SGintermediate) is less than the specific gravity of the outer core layer (SGouter). The specific gravities of the inner core (SGinner) and outer core layer (SGouter) may be substantially the same.

As discussed further below, various polymeric compositions may be used to make the multi-layered and dual-core structures of the golf balls of this invention. The golf balls may contain specific gravity fillers to adjust the weight of the core layers as needed. The amount of fillers and other ingredients used in the compositions is set so that the weight of the golf ball does not exceed limits set by the USGA. The USGA has established a maximum weight of 45.93 g (1.62 ounces). For play outside of USGA rules, the golf balls can be heavier. In one preferred embodiment, the weight of the multi-layered core is in the range of about 28 to about 38 grams.

Core Structure

As discussed above, the core preferably has a multi-layered or dual-layered structure. Preferably, the inner core has a center hardness (CH) within a range having a lower limit of about 38 or 45 or 52 and an upper limit of about 55 or 60 or 62 Shore D. Meanwhile, the intermediate core layer preferably has a surface hardness (ICLSH) within a range having a lower limit of about 46 or 50 or 54 Shore D and an upper limit of about 60 or 64 or 68 Shore D. The outer core layer preferably has a surface hardness (OCLSH) within a range having a lower limit of about 40 or 44 or 48 or 52 Shore D and an upper limit of about 56 or 60 or 64 Shore D. In one embodiment, the surface hardness of the intermediate core layer is greater than the center hardness of the inner core and surface hardness of the outer core layer. In an alternative embodiment, the surface hardness of the intermediate core layer is less than the center hardness of the inner core and surface hardness of the outer core layer.

In one preferred golf ball, the inner core (center) has a “positive” hardness gradient (that is, the outer surface of the inner core is harder than its geometric center) and the outer core layer has a “positive” hardness gradient (that is, the outer surface of the outer core layer is harder than the inner surface of the outer core layer.) In such cases where both the inner core and outer core layer have “positive” hardness gradients, the outer surface hardness of the outer core layer is preferably greater than the material hardness of the inner core (center). In an alternative version, the inner core may have 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,) and the outer core may have a positive hardness gradient. In another version, the inner core (center) has a positive hardness gradient, while the outer core layer has a negative hardness gradient. In yet another version, 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.) Such hardness gradients are further described in Bulpett et al., U.S. Pat. Nos. 7,537,529 and 7,410,429 and Sullivan et al., U.S. Pat. Nos. 7,255,656 and 6,852,044, the disclosures of which are hereby incorporated by reference.

Particularly, the term, “zero hardness gradient” as used herein, means a surface to center (or second surface) 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 (or second surface) 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 (or second surface) 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 (or second surface) 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.

Preferably, the hardness gradient from geometric center of the inner core to the surface of the outer core layer is a positive hardness gradient. That is, the outer surface of the outer core layer is harder than the center of the inner core. Methods for measuring the hardness of the core and cover layers and determining the hardness gradients are discussed in further detail below.
As discussed further below, in a multi-layered core, the inner core and outer core layer, which have relatively high specific gravity levels, may be formed from highly filled thermoplastic or thermoset materials. Meanwhile, the intermediate core layer may be formed of a thermoplastic or thermoset material, which is substantially free of fillers. Preferably, at least one core layer is formed of a rubber or ethylene acid copolymer ionomer composition. The golf balls of this invention having the above-described core constructions show good resiliency (distance) while maintaining a nice feel. The resulting ball has a relatively high COR allowing it to reach 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. At the same time, the ball has a soft feel and good spin control. In the multi-layered core, a portion of the core’s density is distributed towards the center of the ball, that is, some bits of mass of the ball are located relatively close to its axis of rotation. But, not all of the core’s density is distributed towards the center of the ball. Rather, some bits of mass of the ball are located away from its axis of rotation. In general, the Moment of Inertia of a ball (or other object) about a given axis refers to how difficult it is to change the ball’s angular motion about that axis. If the ball’s mass is concentrated towards the center, less force is required to change its rotational rate, and the ball has a relatively low Moment of Inertia. Thereby, the initial spin rate of the ball is increased. Conversely, if the ball’s mass is concentrated towards the outer surface, more force is required to change its rotational rate, and the ball has a relatively low Moment of Inertia. The initial spin rate of the ball is decreased. In the golf balls of this invention, the overall density of the core is generally balanced. Some bits of mass are positioned relatively close to the center of the ball, while other bits of mass are positioned away from the center of the ball. Thus, the ball does not have a relatively high or low Moment of Inertia. Rather, the ball can be described as having a relatively “medium” Moment of Inertia. Thus, the ball has generally good spin control. With a medium spin rate, a professional (or highly skilled) golfer can produce and control the spin of the ball. Such a golfer can make nice approach shots with backspin so the ball stops quickly on the green. At the same time, a recreational (or less skilled) player can strike the ball with the club and still maintain control so that it travels in a relatively straight line. Because of the medium spin rate, the ball will have less side-spin and it is less likely to drift completely off-course. A golfer can get particularly frustrated with their play when they hook or slice the ball, and the high side-spin rate of the ball causes it to land in a neighboring fairway. The average golfer is able to hit the golf balls of this invention with good distance and sense of control. More particularly, as described in Sullivan, U.S. Pat. No. 6,494,795 and Ladd et al., U.S. Pat. No. 7,651,415, the formula for the Moment of Inertia for a sphere through any diameter is given in the CRC Standard Mathematical Tables, 24th Edition, 1976 at 20 (hereinafter CRC reference). In accordance with the above calculations, the Moment of Inertia for a 1.62 oz. golf ball having a diameter of about 1.68 inches with evenly distributed weight through any diameter is about 0.4572 oz·in² (83.6 g·cm²). Such golf balls with a Moment of Inertia substantially higher than this value would be considered relatively high Moment of Inertia golf balls; while golf balls with a substantially lower value would be considered relatively low Moment of Inertia golf balls. Meanwhile, golf balls with substantially the same value would be considered “medium” Moment of Inertia golf balls. In general, such golf balls having a medium Moment of Inertia would have values in the range of about 0.3000 oz·in² to about 0.6000 oz·in².

In addition, the cores of this invention typically have a COR of about 0.75 or greater; and preferably about 0.80 or greater. The compression of the core preferably is about 50 to about 130 and more preferably in the range of about 70 to about 110. Rubber Compositions

Preferably, at least one of the core layers is formed of a rubber composition comprising a rubber material selected from the group of: natural and synthetic rubbers including, but not limited to, polybutadiene, polyisoprene, ethylene propylene rubber ("EPR"), ethylene-propylene-diene ("EPDM") rubber, styrene-butadiene rubber, styrenic block copolymer rubbers (such as "SI", "SIS". "SIB", "SBS"). "SIBS", and the like, where "S" is styrene, "I" is isobutylene, and "B" is butadiene), polyalkenamers such as, for example, polyoctenamer, butyl rubber, halobutyl rubber, polyisoprene elastomers, polyethylene elastomers, polyurethane elastomers, polyurea elastomers, metalloocene-catalyzed elastomers and plastomers, copolymers of isobutylene and α-olefins, halogenated copolymers of isobutylene and polyisobutylene, copolymers of butadiene with acrylonitrile, polychloroprene, alkyl acrylate rubber, chlorinated isoprene rubber, acrylonitrile chlorinated isoprene rubber, and combinations of two or more thereof.

More preferably, the rubber composition comprises polybutadiene. In general, polybutadiene is a homopolymer of 1,3-butadiene. The double bonds in the 1,3-butadiene monomer are attacked by catalysts to grow the polymer chain and form a polybutadiene polymer having a desired molecular weight. Any suitable catalyst may be used to synthesize the polybutadiene rubber depending upon the desired properties. Normally, a transition metal complex (for example, neodymium, nickel, or cobalt) or an alkyl metal such as alkylithium is used as a catalyst. Other catalysts include, but are not limited to, aluminum, boron, lithium, titanium, and combinations thereof. The catalysts produce polybutadiene rubbers having different chemical structures. In a cis-bond configuration, the main internal polymer chain of the polybutadiene appears on the same side of the carbon-carbon double bond contained in the polybutadiene. In a trans-bond configuration, the main internal polymer chain is on opposite sides of the internal carbon-carbon double bond in the polybutadiene. The polybutadiene rubber can have various combinations of cis- and trans-bond structures. A preferred polybutadiene rubber has a 1,4 cis-bond content of at least 40%, preferably greater than 80%, and more preferably greater than 90%. In general, polybutadiene rubbers having a high 1,4 cis-bond content have high tensile strength. The polybutadiene rubber may have a relatively high or low Mooney viscosity.

Examples of commercially available polybutadiene rubbers that can be used in accordance with this invention, include, but are not limited to, BR 01 and BR 1220, available from BOST Elastomers of Bangkok, Thailand; SE BR 1220L A and SE BR 2103, available from DOW Chemical Co of Midland, Mich.; BUDENE 1207, 1207Ts, 1208, and 1280 available from Goodyear, Inc of Akron, Ohio; BR 01, 51 and 730, available from Japan Synthetic Rubber (JSR) of Tokyo, Japan; BUNA CB 21, CB 22, CB 25, CB 24, CB 25, CB 29 MES, CB 60, CB Nd 60, CB 55 NF, CB 70 B, CB KA 8967,
The rubber compositions 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., trimethylol propane 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, calcium, zinc, aluminum, lithium, and nickel. In a particular embodiment, the co-agent is selected from zinc salts of acrylates, diacrylates, methacrylates, and dimethacrylates. In another 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 base rubber.

Radical scavengers such as a halogenated organosulfur, organic disulfide, or inorganic disulfide compounds may be added to the rubber composition. These compounds also may function as “soft and fast agents.” As used herein, “soft and fast agent” means any compound or blend thereof that is capable of making a core: 1) softer (having a lower compression) at a constant “coefficient of restitution” (COR), and/or 2) faster (having a higher COR at equal compression), when compared to a core equivalently prepared without a soft and fast agent. Preferred halogenated organosulfur compounds include, but are not limited to, pentachlorothiophenol (PCTP) and salts of PCTP such as zinc pentachlorothiophenol (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 agent is selected from ZnPCTP, PCTP, ditoly sulfide, diphenyl disulfide, dixylyl disulfide, 2-nitroresorcinol, and combinations thereof.

As discussed above, the compositions of this invention are formulated to have specific gravity values so that they can be used to form certain core components of the golf ball. Particularly, the compositions may contain “fillers” to adjust the specific gravity as needed. As used herein the term “fillers” include any compound or composition that can be used to vary the density or specific gravity of selected portions of the golf ball. Fillers include high-density and low-density fillers.

Suitable specific gravity fillers preferably have specific gravity values in the range from about 2 to about 19, and include, for example, metal (or metal alloy) powder, metal oxide, metal stearates, particulates, carbonaceous materials, and the like or blends thereof. Examples of useful metal (or metal alloy) powders include, but are not limited to, bismuth powder, boron powder, brass powder, bronze powder, cobalt powder, copper powder, Inconel™ metal powder, iron metal powder, molybdenum powder, nickel powder, stainless steel powder, titanium metal powder, zirconium oxide powder, aluminum flakes, tungsten metal powder, beryllium metal powder, zinc metal powder, or tin metal powder. Examples of metal oxides include, but are not limited to, zinc oxide, iron oxide, aluminum oxide, titanium dioxide, magnesium oxide, zirconium oxide, and tungsten trioxide. Examples of particulate carbonaceous materials include, but are not limited to, graphite and carbon black. Examples of other useful fillers
include but are not limited to graphite fibers, precipitated hydrated silica, clay, talc, glass fibers, aramid fibers, mica, calcium metasilicate, barium sulfate, zinc sulfide, silicates, diatomaceous earth, calcium carbonate, magnesium carbonate, regrind (which is recycled uncured center material mixed and ground to 30 mesh particle size), manganese powder, and magnesium powder, 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.

[0044] In a particular aspect of this embodiment, the rubber composition includes filler(s) selected from carbon black, nanoclay (e.g., Cloisite® and Nanofil® nanoclays, commercially available from Southern Clay Products, Inc., and Nanomax® and Nanomer® nanoclays, commercially available from Nanocor, Inc.), talc (e.g., Luzenac HAR® high aspect ratio talcs, commercially available from Luzenac Amerin, Inc.), glass (e.g., glass flake, milled glass, and microglass), mica and mica-based pigments (e.g., Irodon® pearl luster pigments, commercially available from The Merck Group), and combinations thereof.

[0045] In addition, the rubber compositions may include antioxidants to prevent the breakdown of the elastomers. Also, processing aids such as high molecular weight organic acids and salts thereof may be added to the composition. Suitable organic acids are aliphatic organic acids, aromatic organic acids, saturated mono-functional organic acids, unsaturated multifunctional organic acids, multi-unsaturated mono-functional 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, phenoxyacetic acid, naphthalenonic acid, and 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, bismuth, chromium, cobalt, copper, potassium, strontium, 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.)

[0046] 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.

[0047] Other additives and fillers include, but are not limited to, chemical blowing and foaming agents, optical brighteners, coloring agents, fluorescent agents, whitening agents, UV absorbers, light stabilizers, defoaming agents, processing aids, antioxidants, stabilizers, softening agents, fragrance components, plasticizers, impact modifiers, titanium dioxide pigment, acid copolymer wax, surfactants, and fillers, such as zinc oxide, tin oxide, barium sulfate, zinc sulfate, calcium oxide, calcium carbonate, zinc carbonate, barium carbonate, tungsten, tungsten carbide, silica, lead silicate, regrind (recycled material), clay, mica, talc, nano-fillers, carbon black, glass flake, milled glass, and mixtures thereof. Suitable additives are more fully described in, for example, Rajagopal et al., U.S. Patent Application Publication No. 2003/0225197, the entire disclosure of which is hereby incorporated herein by reference. In a particular embodiment, the total amount of filler(s) present in the rubber composition is 15 wt. % or less, or 12 wt. % or less, or 10 wt. % or less, or 9 wt. % or less, or 6 wt. % or less, or 5 wt. % or less, or 4 wt. % or less, or 3 wt. % or less, based on the total weight of the rubber composition.

[0048] Ethylene Acid Copolymers

[0049] Preferably, at least one of the core layers is formed from an ionomer composition comprising an ethylene acid copolymer containing acid groups that are at least partially neutralized. As discussed further below, preferably, the neutralization level is greater than 70%, more preferably at least 90% and even more preferably at least 100%. Suitable ethylene acid copolymers that may be used to form the compositions of this invention are generally referred to as copolymers of ethylene; C3 to C8 α, β-ethylenically unsaturated mono- or dicarboxylic acid; and optional softening monomer. Copolymers may include, without limitation, ethylene acid copolymers, such as ethylene/(meth)acrylic acid, ethylene/(meth)acrylic acid/maleic anhydride, ethylene/(meth)acrylic acid/maleic acid mono-ester, ethylene/maleic acid, ethylene/ maleic acid mono-ester, ethylene(meth)acrylic acid/n-butyl (meth)acrylate, ethylene(meth)acrylic acid/isobutyl (meth)acrylate, ethylene(meth)acrylic acid/methyl (meth)acrylate, ethylene(meth)acrylic acid/ethyl (meth)acrylate terpolymers, and the like. The term, “copolymer,” as used herein, includes polymers having two types of monomers, those having three types of monomers, and those having more than three types of monomers. Preferred α, β-ethylenically unsaturated mono- or dicarboxylic acids are (meth)acrylic acid, ethylenic acid, maleic acid, crotonic acid, fumaric acid, itaconic acid. (Meth)acrylic acid is most preferred. As used herein, (meth)acrylic acid means methacrylic acid and/or acrylic acid. Likewise, (meth)acrylate means methacrylate and/or acrylate.

[0050] When a softening monomer is included, such copolymers are referred to herein as E/X/Y-type copolymers, wherein E is ethylene; X is a C3 to C8 α, β-ethylenically unsaturated mono- or dicarboxylic acid; and Y is a softening monomer. The softening monomer is typically an alkyl (meth)acrylate, wherein the alkyl groups have from 1 to 8 carbon atoms. Preferred E/X/Y-type copolymers are those wherein X is (meth)acrylic acid and/or Y is selected from (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, methyl (meth)acrylate, and ethyl (meth) acrylate. More preferred E/X/Y-type copolymers are ethylene/(meth)acrylic acid/n-butyl acrylate, ethylene/(meth)acrylic acid/methyl acrylate, and ethylene/(meth)acrylic acid/ethyl acrylate.

[0051] The amount of ethylene in the acid copolymer is typically at least 15 wt. %, preferably at least 25 wt. %, and even more preferably at least 40 wt. %, and based on total weight of the copolymer. The amount of C3 to C8 α, β-ethylenically unsaturated mono- or dicarboxylic acid in the acid copolymer is typically from 1 wt. % to 35 wt. %, preferably from 5 wt. % to 30 wt. %, and even more preferably from 5 wt. % to 25 wt. %, and even more preferably from 10 wt. % to 20 wt. %, based on total weight of the copolymer. The amount of optional softening comonomer in the acid copolymer is typically from 0 wt. % to 50 wt. %, preferably from 5 wt. % to 40 wt. %, and even more preferably from 10 wt. % to 35 wt. %,
and even more preferably from 20 wt.% to 30 wt.%, based on total weight of the copolymer. “Low acid” and “high acid” ionomeric polymers, 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 acid moieties, whereas high acid ionomers are considered to be those containing greater than 16 wt.% of acid moieties.

[0052] The acidic groups in the copolymeric ionomers are partially or totally neutralized with a cation source. Suitable cation sources include metal cations and salts thereof, organic amine compounds, ammonium, and combinations thereof. Preferred cation sources are metal cations and salts thereof, wherein the metal is preferably lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, aluminum, manganese, nickel, chromium, copper, or a combination thereof. The metal cation provides the cations capable of neutralizing (at varying levels) the carboxylic acids of the ethylene acid copolymer and fatty acids, if present, as discussed further below. These include, for example, the sulfate, carbonate, acetate, oxide, or hydroxide salts of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, aluminum, manganese, nickel, chromium, copper, or a combination thereof. Preferred metal cation salts are calcium and magnesium-based salts. High surface area cation particles such as micro and nano-scale cation particles are preferred. The amount of cation used in the composition is readily determined based on desired level of neutralization.

[0053] For example, ionomeric resins having acid groups that are neutralized from about 10 percent to about 100 percent may be used. In one ionomer composition, the acid groups are partially neutralized. That is, the neutralization level is from about 10% to about 70%, more preferably 20% to 60%, and most preferably 30% to 50%. These ionomer compositions, containing acid groups neutralized to 70% or less, may be referred to ionomers having relatively low neutralization levels.

[0054] On the other hand, the ionomer composition may contain acid groups that are highly or fully neutralized. These highly neutralized polymers (HNP) are preferred for forming at least one core layer in the present invention. In these HNP, the neutralization level is greater than 70%, preferably at least 90% and even more preferably at least 100%. In another embodiment, an excess amount of neutralizing agent, that is, an amount greater than the stoichiometric amount needed to neutralize the acid groups, may be used. That is, the acid groups may be neutralized to 100% or greater, for example 110% or 120% or greater. In one preferred embodiment, a high acid ethylene acid copolymer containing about 19 to 20 wt. % methacrylic or acrylic acid is neutralized with zinc and sodium cations to a 95% neutralization level.

[0055] “Ionic plasticizers” such as organic acids or salts of organic acids, particularly fatty acids, may be added to the ionomer resin if needed. Such ionic plasticizers are used to make conventional ionomer composition more processable as described in Rajagopalan et al., U.S. Pat. No. 6,756,436, the disclosure of which is hereby incorporated by reference. In one preferred embodiment, the thermoplastic ionomer composition, containing acid groups neutralized to 70% or less, does not include a fatty acid or salt thereof, or any other ionic plasticizer. On the other hand, the thermoplastic ionomer composition, containing acid groups neutralized to greater than 70%, includes an ionic plasticizer, particularly a fatty acid or salt thereof. For example, the ionic plasticizer may be added in an amount of 0.5 to 10 pph, more preferably 1 to 5 pph. The organic acids may be aliphatic, mono- or multifunctional (saturated, unsaturated, or multi-unsaturated) organic acids. Salts of these organic acids may also be employed. Suitable fatty acid salts include, for example, metal stearates, laurate, oleate, palmitate, and the like. For example, fatty acid salts such as zinc stearate, calcium stearate, magnesium stearate, barium stearate, and the like can be used. The salts of fatty acids are generally fatty acids neutralized with metal ions. The metal cation provides the cations capable of neutralizing (at varying levels) the carboxylic acid groups of the fatty acids. Examples include the carbonate, sulfate, acetate and hydroxide salts of metals such as barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, or calcium, and salts thereof. It is preferred the organic acids and salts are 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).

[0056] As noted above, the final ionomer compositions may contain additional materials such as, for example, a small amount of ionic plasticizer, which is particularly effective at improving the processability of highly-neutralized ionomers. For example, the ionic plasticizer may be added in an amount of 0.5 to 10 pph, more preferably 1 to 5 pph. In addition to the fatty acids and salts of fatty acids discussed above, other suitable ionic plasticizers include, for example, polyethylene glycols, waxes, bis-stearamides, minerals, and phthalates. In another embodiment, an amine or pyridine compound is used, preferably in addition to a metal cation. Suitable examples include, for example, ethylamine, methylamine, diethylamine, tert-butylamine, dodecylamine, and the like.

[0057] As discussed above, the ionomer compositions may contain a wide variety of specific gravity fillers to adjust the specific gravity of the composition as needed. High surface area fillers that have an affinity for the acid groups in ionomer may be used. In particular, fillers such as particulate, fibers or flakes having cationic nature such that they may also contribute to the neutralization of the ionomer are suitable. For example, aluminum oxide-containing fillers may be used. Also, silica, fumed silica, or precipitated silica, such as those sold under the tradename HIIISII from PPG Industries, carbon black, and nano-scale materials such as nanotubes, nanoflakes, nanofillers, or nanoclays may be used.

[0058] Other additives and fillers include, but are not limited to, chemical blowing agents, optical brighteners, coloring agents, fluorescent agents, whitening agents, UV absorbers, light stabilizers, defoaming agents, processing aids, antioxidants, stabilizers, softening agents, fragrance components, plasticizers, impact modifiers, TiO2, acid copolymer wax, surfactants, and fillers, such as zinc oxide, tin oxide, barium sulfate, zinc sulfate, calcium oxide, calcium carbonate, zinc carbonate, barium carbonate, tungsten, tungsten carbide, silica, lead silicate, regrind (recycled material), clay, mica, talc, nano-fillers, carbon black, glass flake, milled glass, and mixtures thereof. Suitable additives are more fully described in, for example, Rajagopalan et al., U.S. Patent Application Publication No. 2003/0225197, the entire disclosure of which is hereby incorporated herein by reference. In a particular embodiment, the total amount of additive(s) and filler(s) present in the final thermoplastic ionomeric composition is 15 wt % or less, or 12 wt % or less, or 10 wt % or less,
or 9 wt % or less, 6 wt % or less, or 5 wt % or less, or 4 wt % or less, or 3 wt % or less, based on the total weight of the ionomeric composition.

In another version, the ionomer compositions may contain carbon fibers or fiber sheets comprising a weave of thin carbon fibers held together in a resin. In yet another version, the ionomer compositions may contain a blend of one or more ionomers and a maleic anhydride-grafted non-ionomeric polymer. The non-ionomeric polymer may be a metalloocene-catalyzed polymer. The ionomer compositions may contain a blend of a highly-neutralized ethylene/methacrylic acid copolymer and a maleic anhydride-grafted metalloocene-catalyzed polyethylene. In yet another version, the composition contains a material selected from the group consisting of highly-neutralized ionomers optionally blended with a maleic anhydride-grafted non-ionomeric polymer; polyesters; polyamides; and combinations of two or more thereof.

Cover Structure

The golf ball cores of this invention may be enclosed with one or more cover layers. A wide variety of materials may be used for forming the outer cover including, for example, polyurethanes; polyureas; copolymers, blends and hybrids of polyurethane and polyureas; ethylene acid copolymer ionomer resins (for example, Surlyn® ionomer resins and HPF® 1000 and HPF® 2000, commercially available from DuPont; Iotek® ionomers, commercially available from ExxonMobil Chemical Company; Amplify® IO ionomers of ethylene acrylic acid copolymers, commercially available from The Dow Chemical Company; and Clarico® ionomer resins, commercially available from A. Schulman Inc.); 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; elastomers; flexomers; styrene/butadiene/styrene 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 polyurethane block amides, commercially available from Arkema Inc.; cross-linked trans-polysoprene and blends thereof; polyester-based thermoplastic elastomers, such as Hytrel®, commercially available from DuPont; polyurethane-based thermoplastic elastomers, such as Elastollan®, commercially available from BASF; synthetic or natural vulcanized rubber; and combinations thereof. Castable polyurethanes, polyureas, and hybrids of polyurethanes-polyureas are particularly desirable because these materials can be used to help make a golf ball having high resiliency and a soft feel. By the term, “hybrids of polyurethane and polyurea,” it is meant to include copolymers and blends thereof.

Polyurethanes, polyureas, and blends, copolymers, and hybrids of polyurethane/polyureas are also particularly suitable for forming cover layers. 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.

In one preferred embodiment, the ball includes a dual-cover comprising inner and outer cover layers. The inner cover layer is preferably formed from a composition comprising an ionomer or a blend of two or more ionomers that helps impart hardness to the ball. The inner cover layer preferably has a material hardness of 95 Shore C or less, or less than 95 Shore C or 92 Shore C or less, or 90 Shore C or less, or a material hardness within a range having a lower limit of
60 or 65 or 70 or 75 or 80 or 84 or 85 Shore C and an upper limit of 90 or 92 or 95 Shore C. The thickness of the inner cover layer is preferably within a range having a lower limit of 0.010 or 0.015 or 0.020 or 0.030 inches and an upper limit of 0.035 or 0.045 or 0.080 or 0.120 inches. The outer cover layer preferably has a material hardness of 85 Shore C or less. The thickness of the outer cover layer is preferably within a range having a lower limit of 0.010 or 0.015 or 0.025 inches and an upper limit of 0.035 or 0.040 or 0.055 or 0.080 inches.

In a particular embodiment, the inner cover layer is formed from a composition comprising a high acid ionomer. A particularly suitable high acid ionomer is Surlyn 8150® (DuPont), which is a maleic anhydride-grafted non-ionomer polyethylene. A particularly suitable maleic anhydride-grafted polyethylene is Fusabond 525D® (DuPont), which is a maleic anhydride-grafted, metalloocene-catalyzed ethylene-butene copolymer having about 0.9 wt % maleic anhydride grafted onto the copolymer. A particularly preferred blend of high acid ionomer and maleic anhydride-grafted polyethylene is a 84 wt %/16 wt % blend of Surlyn 8150® and Fusabond 525D®. Blends of high acid ionomers with maleic anhydride-grafted polymers are further disclosed, for example, in U.S. Pat. Nos. 6,392,135 and 6,677,401, the entire disclosures of which are hereby incorporated herein by reference.

In one embodiment, the inner cover layer is formed from a composition comprising a 50/45/5 blend of Surlyn® 8940/Surlyn® 9650/Nurcal® 960. In another embodiment, the inner cover layer is formed from a composition containing about 0.010 to about 0.030 inches, more preferably about 0.020 to about 0.025 inches, and most preferably about 0.020 inches. In this version, the inner cover layer is formed from a partially- or fully-neutralized ionomer having a Shore D hardness of about 55, more preferably greater than about 50, and most preferably greater than about 55. The outer cover layer, in this embodiment, preferably has a thickness of about 0.015 inches to about 0.050 inches, more preferably about 0.020 inches to about 0.030 inches, and most preferably about 0.025 inches. In another multi-layer cover, dual-core embodiment, the outer cover layer is formed from a composition comprising about 0.010 inches to about 0.020 inches, more preferably about 0.010 inches to about 0.015 inches, and most preferably about 0.015 inches. In this version, the outer cover layer has a thickness of about 0.010 inches to about 0.035 inches.

As discussed above, the rubber and ionomer compositions of this invention may be molded to form a multi-layered core that can be used in a variety of ball constructions including, for example, three-piece, four-piece, and five-piece ball designs. For instance, a four-piece ball is shown in FIG. 1, wherein the ball (12) contains a multi-layered core (14) having an inner core (15) and intermediate core layer (15b) and outer core layer (14c) surrounded by a single-layered cover (16). In FIG. 2, the golf ball (18) contains a dual-core (20) having an inner core (21) and outer core layer (20b), and there is no intermediate core layer present. The dual-core is surrounded by a single-layered cover (22). As discussed above, it is preferred that at least one of the core layers is formed from a rubber composition, and at least one of the core layers is formed from a HNP composition comprising an ethylene acid copolymer containing acid groups such that greater than 70% of the acid groups are neutralized. In one particularly preferred version, the inner core is formed from a rubber composition; the intermediate core is formed from the HNP composition; and the outer core is formed from a rubber composition. In an alternative version, a rubber composition is used to form each core layer.

The surfaces of the golf balls shown in FIGS. 1-2 may have various dimple patterns to modify the aerodynamic properties of the ball. It should be understood that the golf balls shown in FIGS. 1-2 are for illustrative purposes only and not meant to be restrictive. Other golf ball constructions can be made in accordance with this invention. For example, the golf ball may contain a multi-layered core, particularly a relatively hard inner cover layer that is softer outer cover layer. The golf ball of this invention may further contain an intermediate layer(s) that is formulated to have specific properties such as layer that helps prevent moisture vapor from penetrating into the core.
outer core layers to produce an intermediate golf ball. The cover layer(s) is subsequently molded over the core to produce a final golf ball.

In compression molding, the outer core and/or inner cover composition is formed into smooth surfaced hemispherical shells which are then positioned around the inner core in a mold having the desired inner cover thickness and subjected to compression molding under heat followed by cooling. This process fuses the shells together to form a unitary intermediate ball. Alternatively, the intermediate balls may be produced by injection molding, wherein the outer core and/or inner cover layer is injected directly around the core placed at the center of an intermediate ball mold under heat and pressure. After molding, the golf balls produced may undergo various further processing steps such as buffing, painting, and marking using conventional techniques.

Test Methods

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 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 aims 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 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 conforms 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 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 hardness (for example, Shore C or Shore D hardness) was measured according to the test method ASTM D-2240.
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 the 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 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 shimmled 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. Compression may be measured as described in McNaMarra et al., U.S. Pat. No. 7,777,871, the disclosure of which is hereby incorporated by reference.

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 is recorded. 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 = \( \frac{V_{out}}{V_{in}} \times \frac{T_{in}}{T_{out}} \)).

When numerical lower limits and numerical upper limits are set forth herein, it is contemplated that any combination of these values may be used. 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. 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.

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.

It is understood that the compositions and golf ball products described and illustrated herein represent only some embodiments of the invention. It is appreciated by those skilled in the art that various changes and additions can be made to compositions and products without departing from the spirit and scope of this invention. It is intended that all such embodiments be covered by the appended claims.

We claim:

1. A golf ball, comprising:
   - a multi-layer core having i) an inner core having a diameter in the range of about 0.015 to about 0.900 inches and specific gravity in the range of about 1.18 to about 5.00 g/cc (SG_{inner});
   - ii) an intermediate core layer having a thickness in the range of about 0.100 to about 0.600 inches and specific gravity in the range of about 0.80 to about 1.20 g/cc (SG_{intermediate}); and
   - iii) an outer core layer having a thickness in the range of about 0.010 to about 0.200 inches and specific gravity in the range of about 1.18 to about 5.00 g/cc (SG_{outer}); so that SG_{inner} is greater than SG_{intermediate}; and SG_{intermediate} is less than SG_{outer}; and
   - a cover having at least one layer.

2. The golf ball of claim 1, wherein the weight of the multi-layer core is in the range of about 28 to about 38 grams.

3. The golf ball of claim 1, wherein at least one of the core layers is formed from a rubber composition comprising a rubber material selected from the group consisting of polybutadiene, ethylene-propylene rubber, ethylene-propylene-diene rubber, polyisoprene, styrene-butadiene rubber, polyalkenamers, butyl rubber, halobutyl rubber, polystyrene elastomers, copolymers of isobutylene and p-alkylstyrene, halogenated copolymers of isobutylene and p-alkylstyrene, copolymers of butadiene with acrylonitrile, polychloroprene, allyl acrylate rubber, chlorinated isoprene rubber, acrylonitrile chlorinated isoprene rubber, and mixtures thereof.

4. The golf ball of claim 3, wherein the rubber composition comprises polybutadiene.

5. The golf ball of claim 4, wherein the polybutadiene rubber composition is used to form the intermediate core layer, wherein the layer has a specific gravity in the range of about 0.93 to about 1.18 g/cc.

6. The golf ball of claim 1, wherein at least one of the core layers is formed from an ionomer composition comprising an ethylene acid copolymer containing acid groups such that greater than 70% of the acid groups are neutralized.

7. The golf ball of claim 6, wherein the ionomer composition is used to form the intermediate core layer, wherein the layer has a specific gravity in the range of about 0.93 to about 0.97 g/cc.

8. The golf ball of claim 1, wherein at least one of the core layers comprises high specific gravity filler selected from the group consisting of metal powder, metal alloy powder, metal oxide, metal stearates, particulates, carbonaceous material, and mixtures thereof.

9. The golf ball of claim 8, wherein the high specific gravity filler is selected from the group consisting of bismuth powder, boron powder, brass powder, bronze powder, cobalt powder, copper powder, iron metal powder, iron metal powder, molybdenum powder, nickel powder, stainless steel powder, titanium metal powder, zirconium oxide powder, aluminum flakes, tungsten metal powder, beryllium metal powder, zinc...
metal powder, tin metal powder, zinc oxide, iron oxide, aluminum oxide, titanium dioxide, magnesium oxide, zirconium oxide and tungsten trioxide.

10. The golf ball of claim 1, wherein the inner core has a diameter in the range of about 0.025 to about 0.080 inches and specific gravity in the range of about 1.20 to about 3.50 g/cc.

11. The golf ball of claim 1, wherein the inner core has a diameter in the range of about 0.030 to about 0.075 inches and specific gravity in the range of about 1.25 to about 3.25 g/cc.

12. The golf ball of claim 1, wherein the intermediate core layer has a diameter in the range of about 0.025 to about 0.080 inches and specific gravity in the range of about 0.090 to about 1.18 g/cc.

13. The golf ball of claim 1, wherein the outer core layer has a thickness in the range of about 0.040 to about 0.170 inches and specific gravity of about 1.10 to about 3.75 g/cc.

14. The golf ball of claim 1, wherein the center of the inner core and surface of the intermediate core layer and surface of the outer core layer each has a hardness, and the surface hardness of the intermediate layer is greater than the center hardness of the inner core and surface hardness of the outer core.

15. The golf ball of claim 1, wherein the center hardness of the inner core is in the range of about 38 Shore D to about 62 Shore D.

16. The golf ball of claim 1, wherein the surface hardness of the intermediate core layer is in the range of about 46 Shore D to about 68 Shore D.

17. The golf ball of claim 1, wherein the surface hardness of the outer core layer is in the range of about 40 Shore D to about 64 Shore D.

18. The golf ball of claim 1, wherein the cover is a single layer having a thickness of about 0.015 to about 0.090 inches and is formed from a thermoplastic or thermoset material.

19. The golf ball of claim 1, wherein the cover comprises two or more layers and has an overall thickness of about 0.020 to about 0.140 inches and wherein each cover layer is formed from a thermoplastic or thermoset material.

20. The golf ball of claim 19, wherein the cover comprises an inner cover layer and outer cover layer, the inner cover having a surface hardness of 60 Shore D or greater and an outer cover layer having a surface hardness in the range of about 20 to about 70 Shore D.

21. The golf ball of claim 20, wherein the inner and outer cover layers are formed from a composition comprising a polymer selected from the group consisting of ethylene acid copolymer ionomers; polyesters; polyamides; polyamide-ethers; polyamide-esters; polyurethanes, polyureas; fluoropolymers; polystyrenes; polypropylene and polyethylene; polyvinyl chlorides; polyvinyl acetates; polycarbonates; polyvinyl alcohols; polyethers; polyimides, polyetherketones, polyimideimides; and mixtures thereof.

22. A golf ball, comprising:

(a) a dual-core having i) an inner core having a diameter in the range of about 0.015 to about 0.900 inches and specific gravity in the range of about 1.18 to about 5.00 g/cc (SG_{inner}); and

(b) an outer core layer having a thickness in the range of about 0.100 to about 0.600 inches and specific gravity in the range of about 0.080 to about 1.20 g/cc (SG_{outer}) so that SG_{inner} is greater than SG_{outer}; and a cover having at least one layer.

23. The golf ball of claim 22, wherein the weight of the dual core is in the range of about 28 to about 38 grams.

24. The golf ball of claim 22, wherein at least one of the core layers is formed from a rubber composition comprising a rubber material selected from the group consisting of polybutadiene, ethylene-propylene rubber, ethylene-propylene-diene rubber, polyisoprene, styrene-butadiene rubber, polyalkenamers, butyl rubber, halobutyl rubber, polyethylene elastomers, copolymers of isobutylene and p-alkylstyrene, halogenated copolymers of isobutylene and p-alkylstyrene, copolymers of butadiene with acrylonitrile, polychloroprene, alkyl acrylate rubber, chlorinated isoprene rubber, acrylonitrile chlorinated isoprene rubber, and mixtures thereof.

25. The golf ball of claim 22, wherein at least one of the core layers is formed from an ionomer composition comprising an ethylene acid copolymer containing acid groups such that greater than 70% of the acid groups are neutralized.