ABSTRACT

Golf ball comprising a core wherein the geometric center has a hardness X of from about 40 Shore C to about 75 Shore C and the first outer surface has a hardness Y of from about 75 Shore C to about 95 Shore C such that (15 Shore C)<(Y−X)≤(55 Shore C). A casing layer, disposed about the core, is formed from a high acid divalent ionomeric composition, and has a second outer surface having a hardness Z of from about 90 Shore C to about 100 Shore C wherein (20 Shore C)<(Z−X)≤(60 Shore C). Core Atti compression A is from about 40 to about 100; Atti compression B of the core and the casing layer, combined, is from about 55 to about 115 such that 1.05≤(B/A)≤1.75; and the overall golf ball Atti compression is from about 65 to about 120. Also, to methods of making the inventive golf balls.
GOLF BALL INCORPORATING CASING LAYER FOR CORE HAVING STEEP HARDNESS GRADIENT AND METHODS RELATING THERETO

FIELD OF THE INVENTION

[0001] This invention relates generally to improved golf ball constructions incorporating casing layers about cores having steep "positive" hardness gradients from geometric center to outer surface.

BACKGROUND OF THE INVENTION

[0002] Solid golf balls are typically made with a solid core encased by a cover. The core may be either a single core or have multiple layers such as a dual core having a solid center and an outer core layer. The cover may be a single layer or be a multi-layered such as a cover having an inner cover layer and an outer cover layer. Additionally, one or more casing layer or intermediate layer may be disposed between the core and the cover.

[0003] Generally, golf ball cores and/or centers are constructed with a thermoset rubber, typically a polybutadiene-based composition. The cores are usually heated and crosslinked to create certain characteristics, such as higher or lower compression, which can impact the spin rate of the ball and/or provide better "feel." These and other characteristics can be tailored to the needs of golfers of different abilities. From the perspective of a golf ball manufacturer, it is desirable to have cores exhibiting a wide range of properties, such as resilience (CoR), durability, spin, and "feel," because this enables the manufacturer to make and sell many different types of golf balls suited to differing levels of ability.

[0004] Toward this end, golf ball manufacturers coordinate the materials of the core, cover and any intermediate layers in order to satisfy the performance needs of skilled and recreational golfers. One such construction is a thermoset rubber-based center or inner core having a steep "positive" hardness gradient from its outer surface to the geometric center, with an outer core layer formed from a different thermoset rubber-based material and having a surface hardness that is less than the center hardness so as to be defined by a "negative" hardness gradient. See, e.g., U.S. Pat. Nos. 7,909,709 and 8,157,674 ("the '709 and '674 patents"), each incorporated by reference herein in its entirety.

[0005] Golf ball manufacturers meanwhile seek to improve golf ball characteristics such as durability in order to build and maintain brand recognition. Durability is an important consideration for many golfers, who expect to be able to play a single quality golf ball for at least an entire round of golf, if not longer. While there is no standard testing method in the golf ball art for evaluating golf ball durability, many tests generally involve repeatedly firing finished golf balls at steel plates that are designed to simulate a golf club face at high speeds (e.g., 135 or 155 ft./sec. or greater). Test balls are typically subjected to 100, 200 or 300 blows or cycles and are inspected for breakage of any sort at regular intervals after each blow, etc.). The more durable a golf ball, the higher the number of blows a golf ball endures before evidencing breakage.

[0006] Accordingly, there is a need for golf balls that are very durable yet may be manufactured cost effectively without sacrificing desired overall golf ball properties such as spin on the driver/wedge, CoR and feel. And in particular, there is such a need for golf ball constructions incorporating cores having a steep positive hardness gradient from geometric center to outer surface. The current invention addresses and fills this need.

SUMMARY OF THE INVENTION

[0007] The invention is directed to a golf ball comprising a core, a cover, and a casing layer disposed between the core and the cover; wherein the core has a first outer surface and a geometric center; the geometric center having a hardness X of from about 40 Shore C to about 75 Shore C and the first outer surface having a hardness Y of from about 75 Shore C to about 95 Shore C such that (15 Shore C)<(Y−X)≤(55 Shore C). The core has an Atti compression A of from about 40 to about 100. The casing layer is formed from a high acid divalent ionic polymer composition and has an inner surface that is adjacent the first outer surface and a second outer surface surrounding the inner surface; the second outer surface having a hardness Z of from about 90 Shore C to about 100 Shore C, wherein (20 Shore C)<(Z−X)≤(60 Shore C). The core and the casing layer, combined, have an Atti compression B of from about 55 to about 115 such that 1.05≤B/A<1.75. The cover has a cover inner surface adjacent the casing layer and a cover outer surface surrounding the cover inner surface, wherein the cover outer surface has a hardness Q of from about 70 Shore C to about 95 Shore C and wherein Q≥Z. The overall golf ball has an Atti compression of from about 60 to about 120.

[0008] In golf balls of the present invention, the core may comprise either a single core (one-piece core) or a multi-piece core comprising a center surrounded by one or more outer core layers. Additionally, the intermediate layer and/or cover may each comprise one or more layers.

[0009] As used herein, the term "high acid" ionomers refers to ionic copolymers or terpolymers of an olefin having from about 2 to 8 carbon atoms and a carboxylic acid having from about 3 to 8 carbon atoms, with an acid content of at least about 16% by weight. Preferably, the carboxylic acid content in the ionomer is from about 18% to about 7%, and more preferably from about 18% to about 22%. The carboxylic acid may be an unsaturated monocarboxylic acid such as acrylic, methacrylic, crotonic, maleic, fumaric, or itaconic acid. At least about 10% by weight of the carboxylic acid groups are neutralized with a metal cation such as sodium, lithium, zinc, magnesium, etc. Preferably, between about 30% and about 100% of the carboxylic acid groups are neutralized.

Examples of high-acid ionomers include copolymers of ethylene and acrylic acid or methacrylic acid. Optionally, a softening comonomer may be incorporated to produce an ionic-meric terpolymer. The comonomer includes vinyl esters of aliphatic carboxylic acids wherein the acid has 2 to 10 carbon atoms, alkyl ethers wherein the alkyl group has 1 to 10 carbon atoms, alkyl acrylates wherein the alkyl group has 1 to 10 carbon atoms, or alkyl acrylateacrylates such as alkyl methacrylates wherein the alkyl group has 1 to 10 carbon atoms. Examples of the comonomer include vinyl acetate, methyl acrylate, methallyl methacrylate, ethyl acrylate, ethyl methacrylate, iso-butyl acrylate, n-butyl acrylate, butyl methacrylate, or the like.

[0010] High-acid ionomers are commercially available from several different manufacturers. For example, copolymers of ethylene and methacrylic acid are produced by E. I. DuPont de Nemours & Company under the trademark of Surlyn®; ionic copolymers and terpolymers of ethylene and acrylate are produced by ExxonMobil Chemical under the
trademarks of Escor®, and Iotek®, filler-modified poly(ethylene-methacrylic acid) ionomers are produced by DuPont under the trademark of Bexloy®, ionomeric polyethylene copolymers are produced by A. Schulman Inc. under the trademark of Formion®, and polyolefin ionomers are produced by Diamond & Network Polymers, Inc. Exemplary high-acid ionomers include Surlyn® 6120, 8140, 8150, 9120, 9150, and certain high-flow ionomers that are under development. Preferably, the high-acid ionomers have a mole percent acid content of at least 5.5%, a flexural modulus of at least 50,000 psi, a Shore D hardness of at least about 60, a Vicat softening point of at least about 50°F, a melting point of at least about 80°F, and a freezing point of less than about 55°F.

In one embodiment, the high acid divalent ionomeric composition has been neutralized with a divalent cation selected from the group consisting of zinc, magnesium and calcium, and blends thereof. For example, the high acid divalent ionomeric composition may comprise an ethylene/methacrylic acid (E/MAA) copolymer having 19% MAA as seen in Examples 1 and 2 of TABLES I and II hereinafter.

The high acid divalent ionomeric composition may be filled with a reinforcing material in order to further reduce spin and improve durability. The reinforcing material may be selected from fibers, flakes, flakes, glass flakes, microballoons, glass fibers, polymeric fiber, polymeric flocks, silica and clay, for example. The reinforcing material may be included in an amount of from about 2 parts to about 40 parts of the total casing composition. In one embodiment, the filler is present in an amount of from about 2 parts to about 9 parts of the casing material. In another embodiment, the filler is present in an amount of from about 10 parts to about 19 parts of the casing material. In yet another embodiment, the filler is present in an amount of from about 20 parts to about 29 parts of the casing material. In still another embodiment, the filler is present in an amount of from about 3 parts to about 39 parts of the casing material. In an alternative embodiment, the filler is in an amount of from about 1 parts to about 5 parts of the casing material.

Several non-limiting examples are as follows. In one embodiment, hardness X is from about 45 Shore C to about 70 Shore C, Y is from about 77 Shore C to about 86 Shore C and Z is from about 90 Shore C to about 94 Shore C. In this embodiment, hardness Q may be from about 75 Shore C to about 94 Shore C, for example. In another embodiment, hardness X is from about 55 Shore C to about 74 Shore C, Y is from about 81 Shore C to about 90 Shore C and Z is from about 93 Shore C to about 96 Shore C. And hardness Q may be from about 80 Shore C to about 95 Shore C, for example. In yet another embodiment, hardness X is from about 65 Shore C to about 68 Shore C, Y is from about 84 Shore C to about 89 Shore C and Z is from about 97 Shore C to about 99 Shore C. In this embodiment, hardness Q may be from about 85 Shore C to about 95 Shore C, for example.

Other examples consistent with the construction of a golf ball of the invention are as follows. Where hardness X is at least 15 Shore D but less than 25 Shore D, then hardness Y is at least 35 Shore D but less than 60 Shore D. Where hardness X is 25 Shore D, then hardness Y is greater than 35 Shore D and up to about 65 Shore D. Where hardness X is 31 Shore D, then hardness Y is greater than 41 Shore D and up to about 65 Shore D. Where hardness X is 50 Shore D, then hardness Y is greater than 60 Shore D and up to about 65 Shore D. Where hardness X is 5 Shore C to less than 70 Shore C, then hardness Y may be from about 75 Shore C to about 95 Shore C. Where hardness X is 60 Shore C, then hardness Y must be greater than 75 Shore C and may be up to about 95 Shore C. Where hardness X is 61 Shore C, then hardness Y is greater than 76 Shore C and up to about 95 Shore C. Where hardness X is 75 Shore C, then hardness Y is greater than 90 Shore C and up to about 95 Shore C. Where hardness X is from 40 Shore C to less than 70 Shore C, then hardness Y may be at least 90 Shore C and up to about 100 Shore C. Where hardness X=70 Shore C, then Z>90 Shore C.

In another embodiment, a golf ball of the invention comprises a core, a cover, and a casing layer disposed between the core and the cover, wherein the core has a first outer surface and a geometric center; the geometric center having a hardness X of from about 15 Shore D to about 54 Shore D and the first outer surface having a hardness Y of from about 35 Shore D to about 65 Shore D such that (10 Shore D)<(Y-X)<=35 Shore D). The casing layer is formed from a high acid divalent ionomeric composition and has an inner surface that is adjacent the first outer surface and a second outer surface surrounding the inner surface; the second outer surface having a hardness Z of from about 60 Shore D to about 75 Shore D; wherein (10 Shore D)<(Z-X)<=35 Shore D). The core has an Atti compression A of from about 40 to about 100. The core and the casing layer, combined, have an Atti compression B of from about 55 to about 115 such that 1.05s(Att/A)s1.75. The cover has a cover inner surface adjacent the casing layer and a cover outer surface surrounding the cover inner surface wherein the cover outer surface has a hardness Q of from about 50 Shore D to about 68 Shore D and wherein QsZ. The overall golf ball an Atti compression of from about 60 to about 120.

Several non-limiting examples as follows. In one embodiment, hardness X is from about 20 Shore D to about 45 Shore D, Y is from about 35 Shore D to about 56 Shore D and Z is from about 62 Shore D to about 73 Shore D. In this embodiment, hardness Q may be from about 59 Shore D to about 65 Shore D, for example, as long as QsZ. In another embodiment, hardness X is from about 30 Shore D to about 40 Shore D, Y is from about 41 Shore D to about 54 Shore D and Z is from about 65 Shore D to about 71 Shore D. In this embodiment, hardness Q may be from about 55 Shore D to about 65 Shore D, as long as QsZ. In yet another embodiment, hardness X is from about 35 Shore D to about 38 Shore D, Y is from about 48 Shore D to about 50 Shore D and Z is from about 68 Shore D to about 73 Shore D. In this embodiment hardness Q is from about 60 Shore D to about 65 Shore D, for example, and therefore always wherein QsZ.

Other examples consistent with the construction of a golf ball of the invention are as follows. Where hardness X is at least 15 Shore D but less than 25 Shore D, then hardness Y is at least 35 Shore D but less than 60 Shore D. Where hardness X is 25 Shore D, then hardness Y is greater than 35 Shore D and up to about 65 Shore D. Where hardness X is 31 Shore D, then hardness Y is greater than 41 Shore D and up to about 65 Shore D. Where hardness X is 50 Shore D, then hardness Y is greater than 60 Shore D and up to about 65 Shore D. Where hardness X is 5 Shore C to less than 70 Shore C, then hardness Y may be from about 75 Shore C to about 95 Shore C. Where hardness X is 60 Shore C, then hardness Y must be greater than 75 Shore C and may be up to about 95 Shore C. Where hardness X is 61 Shore C, then hardness Y is greater than 76 Shore C and up to about 95 Shore C. Where hardness X is 75 Shore C, then hardness Y is greater than 90 Shore C and up to about 95 Shore C. Where hardness X is from 40 Shore C to less than 70 Shore C, then hardness Y may be at least 90 Shore C and up to about 100 Shore C. Where hardness X=70 Shore C, then Z>90 Shore C.

The invention also relates to a method of making a golf ball of the invention comprising: providing a core; wherein the core has a first outer surface and a geometric center; the geometric center having a hardness X of from about 40 Shore C to about 75 Shore C and the first outer
surface having a hardness Y of from about 75 Shore C to about 95 Shore C such that (15 Shore C)<(Y-X)<(55 Shore C); and wherein the core has an Atti compression A of from about 40 to about 100; forming a casing layer about the core; wherein the casing layer is formed from a high acid divalent ionomer composition and has an inner surface that is adjacent the first outer surface and a second outer surface surrounding the inner surface; the second outer surface having a hardness Z of from about 90 Shore C to about 100 Shore C; wherein (20 Shore C)<(Z-X)<(55 Shore C); and wherein the core and the casing layer, combined, have an Atti compression B of from about 55 to about 115 such that 1.05≤(B/A)≤1.75; and forming a cover about the casing layer such that the finished golf ball has an Atti compression of from about 60 to about 120.

[0019] In a different embodiment, the invention relates to a method of making a golf ball of the invention comprising: providing a core; wherein the core is formed from a substantially homogenous composition throughout and has a first outer surface and a geometric center; the geometric center having a hardness X' of from about 15 Shore D to about 54 Shore D and the first outer surface having a hardness Y' of from about 35 Shore D to about 65 Shore D such that (10 Shore D)<(Y'-X')<(55 Shore D); and wherein the core has an Atti compression A of from about 40 to about 100; forming a casing layer about the core; wherein the casing layer is formed from a high acid divalent ionomer composition and has an inner surface that is adjacent the first outer surface and a second outer surface surrounding the inner surface; the second outer surface having a hardness Z' of from about 60 Shore D to about 75 Shore D; wherein (10 Shore D)<(Z'-X')<(55 Shore D); and wherein the core and the casing layer, combined, have an Atti compression B of from about 55 to about 115; such that 1.05≤(B/A)≤1.75; and forming a cover about the casing layer such that the finished golf ball has an Atti compression of from about 60 to about 120.

[0020] In a different embodiment, the core is formed from a substantially homogenous composition throughout and/or the casing layer is formed from a substantially homogenous composition throughout.

[0021] Further embodiments are envisioned wherein the term “comprising” in each of the embodiments above is replaced with the term “consisting essentially of” or “consisting of”.

**DETAILED DESCRIPTION OF THE INVENTION**

[0022] Golf balls of the invention exhibit excellent durability yet may be manufactured cost effectively without sacrificing desired overall golf ball properties such as spin on the driver/wedge, CoR and feel. The following prophetic examples illustrate some of the benefits provided by a golf ball of the invention over conventional golf balls. In this regard, TABLE I below displays the constructions and properties for two prophetic inventive golf balls Ex. 1 and Ex. 2 and four comparative prophetic golf balls Comp. Ex. 1, Comp. Ex. 2, Comp. Ex. 3, and Comp. Ex. 4:

<table>
<thead>
<tr>
<th>TABLE I</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Core type</td>
</tr>
<tr>
<td>Center Formulation</td>
</tr>
<tr>
<td>Core (inches)</td>
</tr>
<tr>
<td>Outer Core Diameter (inches)</td>
</tr>
<tr>
<td>Atti Compression A</td>
</tr>
<tr>
<td>Core Hardness X (Shore C)</td>
</tr>
<tr>
<td>Surface Hardness Y (Shore C)</td>
</tr>
<tr>
<td>Casing</td>
</tr>
<tr>
<td>Surlin 9120 (Zn)</td>
</tr>
<tr>
<td>Surlin 9440 (Li)</td>
</tr>
<tr>
<td>Surlin 9240 (Na)</td>
</tr>
<tr>
<td>Surlin 9565 (Zn)</td>
</tr>
<tr>
<td>Akroback ND 110</td>
</tr>
<tr>
<td>Casing Diameter (inches)</td>
</tr>
<tr>
<td>Atti Compression B</td>
</tr>
<tr>
<td>Shore C Surface Hardness Z (Shore C)</td>
</tr>
<tr>
<td>Ball</td>
</tr>
<tr>
<td>Cover Type</td>
</tr>
<tr>
<td>Cover Hardness Q (Shore C)</td>
</tr>
<tr>
<td>Atti Compression</td>
</tr>
<tr>
<td>CoR</td>
</tr>
<tr>
<td>Durability - 1st</td>
</tr>
<tr>
<td>Driver Spin</td>
</tr>
<tr>
<td>Core Gradient</td>
</tr>
</tbody>
</table>
Further, each of the golf balls identified in TABLE I are formed from either: a dual core having a center formed from Core formulation A surrounded by an outer core layer formed from Core formulation B as detailed in TABLE II below; or a single core formed from Core formulation C as also detailed in TABLE II:

TABLE II

<table>
<thead>
<tr>
<th>Formulation</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybutadiene</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Zinc diacylate</td>
<td>21</td>
<td>37</td>
<td>32</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Peroxide</td>
<td>0.6</td>
<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>Regiard</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Barium Sulfate</td>
<td>18</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>Zinc pentachloroethylenol</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Cure Temp. (°E)</td>
<td>355</td>
<td>355</td>
<td>330</td>
</tr>
<tr>
<td>Cure Time (min.)</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
</tbody>
</table>

All golf balls of TABLE I, except for golf ball Comp. Ex. 4, include a dual core having a 1.55 inch diameter and comprising a 1 inch center (formula A) surrounded by an outer core layer (formula B). See TABLE II. The dual core has a geometric center hardness of 52 Shore C and a first outer surface hardness Y of 89 Shore C. Thus, the dual core arrangement has a steep positive hardness gradient from geometric center to outer surface (Y-X) of 37 Shore C. See TABLE I. Golf ball Comp. Ex. 4, meanwhile, incorporates a single core (formula C) having a diameter of 1.55 inches see TABLE II. This single core has a geometric center hardness of 70 Shore C and a first outer surface hardness Y of 78 Shore C. Accordingly, the single core has a positive hardness gradient of 8 Shore C from geometric center to outer surface.

All of the golf balls of TABLE I incorporate cores having a geometric center hardness X and a first outer surface hardness Y that are within the widest required ranges for hardness X and hardness Y (namely hardness X of from about 40 Shore C to about 75 Shore C and hardness Y of from about 75 Shore C to about 95 Shore C). However, while the golf balls of Ex. 1, Ex. 2, Comp. Ex. 1, Comp. Ex. 2 and Comp. Ex. 3 incorporate cores having a hardness gradient (Y-X) that is within the required hardness gradient range for cores in golf balls of the invention, namely (15 Shore C)-(Y-X) ≦ (55 Shore C), notably, the core in golf ball Comp. Ex. 4 has a hardness gradient Y-X of 8 Shore C, which is undesirably outside the required hardness gradient range for cores in golf balls of the invention.

The casing layers of golf ball Ex. 1 and Comp. Ex. 4 are identical, each being formed from a high acid, divalent, low flow ionomer, namely Surlyn®9120 (Zn). Meanwhile, the casing layers for golf balls Ex. 2, Comp. Ex. 1, Comp. Ex. 2 and Comp. Ex. 3 differ from those of golf balls Ex. 1 and Comp. Ex. 4 in at least one of the following respects: (1) by acid content level; (2) by cation type(s); and/or (3) further incorporating filler.

For example, the casing layer of golf ball Ex. 2, while formed from Surlyn®9120 (Zn), further incorporates 10 parts of Arkote®%ND 109, a very fine, chopped nylon fiber from Arkotech, Comp. Next, the casing layer of golf ball Comp. Ex. 1 is formed from a 50/50 blend of Surlyn®87940 (Li) and Surlyn®8940 (Na), both being medium acid, but monovalent and medium flow ionomers. Additionally, the casing layer of golf ball Comp. Ex. 2 is formed from Surlyn®88150 (Na, a high acid but a monovalent and high flow ionomer. Finally, the casing layer of golf ball Comp. Ex. 3 is formed from a 50/50 blend of Surlyn®9650 (Zn), a divalent but low acid and high flow ionomer, with Surlyn®9840 (Na), a medium acid but monovalent and medium flow ionomer.

All of the casing layers, except for that of golf ball Comp. Ex. 3, have a second outer surface hardness Z that is within the widest required range for Z of from about 90 Shore C to about 100 Shore C. In particular, both golf balls Ex. 1 and Comp. Ex. 4, being identical, have a second outer surface hardness (Z) of 93 Shore C. Golf ball Ex. 2, having a casing layer that is filled but is otherwise identical to the casing layers of golf balls Ex. 1 and Comp. Ex. 4, has a second outer surface hardness Z of 95 Shore C—greater than that of the unfilled casing layers of golf balls Ex. 1 and Comp. Ex. 4. Meanwhile, golf balls Comp. Ex. 1 and Comp. Ex. 2 have second outer surface hardness Z's of 96 shore C and 97 Shore C, respectively. Finally, the second outer surface hardness of golfball Comp. Ex. 3's noneforming casing layer is undesirably 87.

For each golf ball in TABLE I, Z-X falls within the widest required range of (20 Shore C)<(Z-X)<(60 Shore C). Similarly, B/A, for all golf balls, is likewise within the widest required range of 1.05≦(B/A)<1.75. Meanwhile, Q is within the widest required range of from about 70 Shore C to about 95 Shore C for all golf balls of TABLE I as well. And the requirement of QaZ is satisfied for every golf ball of TABLE I except for golf ball Comp. Ex. 3.

The durability of each golf ball may be evaluated by any procedure known in the art for evaluating durability. For example, the following procedure may be used for indicating a durability failure. Each test golf ball may be continuously
fired at 155 feet/second (ft/s) through light gates into a steel plate until the measured outbound and inbound times (CoR @ 155 ft/s) drops by 0.025 points.

[0031] Spin off the driver/wedge may be assessed by a driver set-up of 12° at 165 mph and a wedge set-up* of 24.5° at 95 mph.

[0032] Accordingly, the resulting durability and spin of golf balls Ex. 1, Ex. 2, Comp. Ex. 1, Comp. Ex. 2, Comp. Ex. 3 and Comp. Ex. 4 as shown in TABLE 1 above may be compared. In this regard, comparing the resulting spin and durability of golf balls Ex. 1 and Ex. 2 with those of golf balls Comp. Ex. 1, Comp. Ex. 2, Comp. Ex. 3 and Comp. Ex. 4 reveals that desirable lower spin and better durability may be achieved in golf balls Ex. 1 and Ex. 2 incorporating a core having a steep hardness grade as defined herein surrounded by a casing layer formed from a substantially homogenous high acid divalent ionomeric composition as also defined herein.

[0033] Further, a comparison of the resulting spin and durability of golf ball Ex. 1 with those of golf ball Ex. 2 illustrates how filling the substantially homogenous high acid divalent ionomeric composition may further reduce golf ball spin and further improve durability of the resulting golf ball having a steep gradient core by layer incorporating a substantially homogenous high acid divalent ionomeric composition containing casing layer.

[0034] Even further, observing golf ball Ex. 1’s resulting lower spin than that of golf ball Comp. Ex. 4 demonstrates how the widest required Y–X hardness gradient range for a core of a golf ball of the invention—namely (15 Shore C)<(Y–X)≤(55 Shore C)—is important in simultaneously achieving both reduced golf ball spin and improved golf ball durability since Y–X for golf ball Comp. Ex. 4 is 8 Shore C, outside the required widest hardness gradient range defined herein for a core in a golf ball of the invention.

[0035] Golf balls of the present invention include a core surrounding by at least one casing layer, which is surrounded by at least one cover layer. A golf ball of the invention may have any overall diameter, but a generally preferred diameter is 1.68 inches — which meets the USGA (United States Golf Association) standard.

[0036] A core in a golf ball of the invention may be a solid single core. Alternatively, the core may be a multi-layered core comprising a center and at least one outer core layer. The center of the core may be solid, liquid-filled or hollow sphere. A core may be surrounded by one or more intermediate and/or cover layers. A core may even include a solid or liquid center around which tensioned elastomeric material is wound.

[0037] The core in a golf ball of the invention if a single core may have a diameter of about 1.0 inch to about 1.64 inches, or about 1.30 inches to about 1.620, or about 1.40 inches to about 1.60 inches.

[0038] Cores for the golf balls of the present invention may alternatively have an outer core layer formed about a center, referred to as a “dual core” arrangement. In a multi-layer embodiment, the center has an outer diameter of about 0.25 inches to about 1.40 inches, or about 0.8 inches to about 1.30 inches, or about 1.00 inches to about 1.20 inches. The core may have an outer diameter of about 1.40 inches to about 1.64 inches, or about 1.50 inches to about 1.60 inches, or about 1.53 inches to about 1.58 inches.

[0039] The casing layer disposed about the core may have a thickness of from about 0.015 inches to about 0.250 inches. In turn, the cover may have a thickness of from about 0.015 inches to about 0.100 inches.

[0040] The core has a steep “positive” hardness gradient from core geometric center to core outermost surface. The term steep “positive” hardness gradient, as used herein, refers to the outermost surface of the core having a hardness that is greater than the hardness of the core geometric center by greater than about 15 Shore C but less than about 55 Shore C or greater than about 10 Shore D but less than about 35 Shore D. In a different embodiment, the term steep “positive” hardness gradient, as used herein, refers to the outermost surface of the core having a hardness that is greater than the hardness of the core geometric center by greater than 15 Shore C but less than 55 Shore C or greater than 10 Shore D but less than 35 Shore D.

[0041] The center of the core may be solid or even liquid-filled or gas filled as long the hardness of the core geometric center is less than the hardness of the core outer surface as defined herein. In an embodiment wherein the core comprises a center or inner core surrounded by an outer core layer, the steep hardness gradient is between the hardness of the geometric center and the hardness of the outermost layer of the outermost core layer.

[0042] 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.

[0043] The hardness of a core may be measured by taking measurements at the surface of the core and radially inward towards the center of the core, typically at 2-mm increments. As used herein, the terms “negative” and “positive” refer to the result of subtracting the hardness value at the innermost portion of the component being measured (e.g., the center of a core) from the hardness value at the outer surface of the component being measured (e.g., the outer surface of the single core or the outer surface of an outer core layer in a dual core arrangement, etc.).

[0044] The center hardness of a core and the outer surfaces of a single core or outer core layer in a multi-layer core arrangement are readily determined according to the procedures given herein, if the measurement is made prior to surrounding the layer with an additional core layer.

[0045] 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, so that a different procedure detailed below may be used for measuring a point located 1 mm from an interface is used. The hardness of a golf ball layer at a point located 1 mm from an interface is obtained according to the following procedure. First, an axis defining the geometric center of the core is revealed by preparing the core according to the above procedure for measuring the center hardness of a core. Leaving the core in the holder, a point located 1 mm radially inward or outward from the interface of two layers is determined and marked, and the hardness thereof is measured according to ASTM D-2240.

[0046] 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 indentor before a surface hardness reading is obtained. A calibrated, digital durometer, capable of reading to 0.1 hardness units is used for all hardness measurements and the maximum reading is obtained. 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.

[0047] Preferably the core layers (center or outer core layer) are made from a composition including at least one thermoset base rubber, such as a polybutadiene rubber, cured with at least one peroxide and at least one reactive co-agent, which can be a metal salt of an unsaturated carboxylic acid, such as acrylic acid or methacrylic acid, a non-metallic coagent, or mixtures thereof. Preferably, a suitable antioxidant is included in the composition. An optional soft and fast agent (and sometimes a cis-to-trans catalyst), such as an organosulfur or metal-containing organosulfur compound, can also be included in the core formulation. Other ingredients that are known to those skilled in the art may be used, and are understood to include, but not be limited to, density-adjusting fillers, process aids, plasticizers, blowing or foaming agents, sulfur accelerators, and/or non-peroxide radical sources.

[0048] The base thermoset rubber, which can be blended with other rubbers and polymers, typically includes a natural or synthetic rubber. A preferred base rubber is 1,4-polybutadiene having a cis structure of at least 40%, preferably greater than 80%, and more preferably greater than 90%.

[0049] Examples of desirable polybutadiene rubbers include BUNA® CB22, BUNA® CB23, BUNA® CB1221, BUNA® CB1220, and BUNA® CB1203, commercially available from LANXESS Corporation; UBEPOL® 360L and UBEPOL® 150L and UBEPOL® BR rubbers, commercially available from UBE Industries, Ltd. of Tokyo, Japan; KINEX® 7245 and KINEX® 7265 Budene 1207, Budene 1208, and Budene 1280, commercially available from Good-year of Akron, Ohio; SE BR-1220, commercially available from Dow Chemical Company; EUROPRENE® NEOCIS® BR 40 and BR 60, commercially available from Polimeri Europe; and BR 01, BR 730, BR 735, BR 11, and BR 51, commercially available from Japan Synthetic Rubber Co., Ltd; PETROFLEX® BRNd-40; KARBOCHEM® ND40, ND45, and ND60, commercially available from KARBOCHEM; and SE BR-1220, commercially available from The Dow Chemical Company.

[0050] Rubber compositions of the present invention may in some embodiments include a resorcinol to form the steep “positive” hardness gradient core. Preferred resorcinols include compounds represented by the following formula, and hydrates thereof:

\[
\begin{align*}
R_1 & \quad \text{wherein each } R_1, R_2, R_3, \text{ and } R_4 \text{ is independently selected from the group consisting of hydrogen, a halogen group (F, Cl, Br), an alkyl group, a carboxyl group } (-\text{COOH}) \text{ and metal salts thereof (e.g., } -\text{COO' M}^+ \text{) and esters thereof } (-\text{COOR}, \text{ an acetoxy group } (-\text{COOCH}_3), \text{ a halogenated carbonyl group } (-\text{COX}), \text{ a sulfo group } (-\text{SO}_2\text{H}), \text{ and esters thereof } (-\text{SO}_2\text{R}), \text{ a halogenated sulfonate group } (-\text{SO}_3\text{X}) \text{, a sulfino group } (-\text{SO}_3\text{H}), \text{ an alkylsulfonyl group } (-\text{SOR}), \text{ a carbamoyl group } (-\text{CONH}_2)) \text{, a halogenated alkyl group, a cyanogroup } (-\text{CN}), \text{ an alkoxy group } (-\text{OR}), \text{ a hydroxy group } (-\text{OH}) \text{ and metal salts thereof (e.g., } -\text{O'M}^+ \text{), an amino group } (-\text{NH}_2), \text{ a nitro group } (-\text{NO}_2), \text{ an aryl group (e.g., phenyl, tolyl etc.), an arylox group (e.g., phenoxy, etc.), an arylalkyl group (e.g., cumyl } (-\text{C(CH}_3}_2\text{phenyl}), \text{ benzyl } (-\text{CH}_3\text{phenyl})), \text{ a nitroso group } (-\text{NO}), \text{ an acetalimidogroup } (-\text{NCOCH}_3), \text{ and a vinyl group } (-\text{CH=CH}_2). \text{ 2-Nitroresorcinol is particularly preferred.}
\end{align*}
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[0051] The base rubber may also comprise high or medium Mooney viscosity rubber, or blends thereof. A “Mooney” unit is a unit used to measure the plasticity of raw or unvulcanized rubber. The plasticity in a “Mooney” unit is equal to the torque, measured on an arbitrary scale, on a disk in a vessel that contains rubber at a temperature of 100°C and rotates at two revolutions per minute. The measurement of Mooney
viscosity is defined according to ASTM D-1646. The Mooney viscosity range is preferably greater than about 40, more preferably in the range from about 40 to about 80 and more preferably in the range from about 40 to about 60. Polybutadiene rubber with higher Mooney viscosity may also be used, so long as the viscosity of the polybutadiene does not reach a level where the high viscosity polybutadiene clogs or otherwise adversely interferes with the manufacturing machinery. It is contemplated that polybutadiene with viscosity less than 65 Mooney can be used with the present invention. In one embodiment of the present invention, golf ball cores made with mid- to high-Mooney viscosity polybutadiene material exhibit increased resiliency (and, therefore, distance) without increasing the hardness of the ball. Such cores are soft, i.e., compression less than about 60 and more specifically in the range of about 50-55. Cores with compression in the range of from about 30 to about 50 are also within the range of this preferred embodiment. Commercial sources of suitable mid- to high-Mooney viscosity polybutadiene include Bayer AG CB23 (Nd-catalyzed), which has a Mooney viscosity of around 50 and is a highly linear polybutadiene, and CB 1203 (Co-catalyzed). If desired, the polybutadiene can also be mixed with other elastomers known in the art, 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. In one preferred embodiment, the base rubber comprises a Nd-catalyzed polybutadiene, a rare earth-catalyzed polybutadiene rubber, or blends thereof. If desired, the polybutadiene can also be mixed with other elastomers known in the art such as natural rubber, polyisoprene rubber and/or styrene-butadiene rubber in order to modify the properties of the core. Other suitable base rubbers include thermosetting materials such as, ethylene propylene diene monomer rubber, ethylene propylene rubber, butyl rubber, halobutyl rubber, hydrogenated nitrile butadiene rubber, nitrile rubber, and silicone rubber.

Thermoplastic elastomers (TPE) many 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 rubber, styrene-isoprene-styrene, etc., a metallocone 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 PERAX®, 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 TPU's above may also contain functionality suitable for grafting, including maleic acid or maleic anhydride.

Additional polymers may also optionally be incorporated into the base rubber. Examples include, but are not limited to, thermoset elastomers such as core regrind, thermoplastic vulcanize, copolymeric ionomer, terpolymeric ionomer, polycarbonate, polyamide, copolymeric polyamide, polyster, polyvinyl alcohol, acrylonitrile-butadiene-styrene copolymers, polyurethane, polycarbonate, polyphenylene ether, impact-modified polyphenylene ether, high impact polystyrene, diallyl phthalate polymer, styrene-acrylonitrile polymer (SAN) (including olefin-modified SAN and acrylonitrile-styrene-acrylonitrile polymer), styrene-maleic anhydride copolymer, styrenic copolymer, functionalized styrenic copolymer, functionalized styrenic terpolymer, styrenic terpolymer, cellulose polymer, liquid crystal polymer, ethylene-vinyl acetate copolymers, polystyrene, and polyisobutylene or any metallocone-catalyzed polymers of these species.

Suitable peroxide initiating agents include dicumyl peroxide; 2,5-dimethyl-2,5-di(t-butylperoxy) hexene; 2,5-dimethyl-2,5-di(t-butylperoxy) hexene; 2,5-dimethyl-2,5-di((benzoylperoxy)hexene; 2,2′-bis(t-butylperoxy)-di-iso-propylbenzene; 1,1-bis(t-butylperoxy)-3,3,5-trimethyl cyclohexane; n-butyl 4,4′-bis(t-butylperoxy)valerate; t-butyl perbenzoate; benzoyl peroxide; n-butyl 4,4′-bis(butylperoxy) valerate; di-t-butyl peroxide; or 2,5-di-(t-butylperoxy)-2,5-dimethyl hexane, lauryl peroxide, t-butyl hydroperoxide, c-c′-bis(t-butylperoxy)diisopropylbenzene, di(2-t-butylperoxy-isopropyl)benzene, di-t-amyl peroxide, di-t-butyl peroxide. Preferably, the rubber composition includes from about 0.25 to about 5.0 parts by weight peroxide per 100 parts by weight rubber (phr), more preferably 0.5 phr to 3 phr, most preferably 0.5 phr to 1.5 phr. In a most preferred embodiment, the peroxide is present in an amount of about 0.8 phr. These ranges of peroxide are given assuming the peroxide is 100% active, without accounting for any carrier that might be present. Because many commercially available peroxides are sold along with a carrier compound, the actual amount of active peroxide present must be calculated. Commercially-available peroxide initiating agents include DICUP™ family of dicumyl peroxides (including DICUP™ R, DICUP™ 40C and DICUP™ 440KE) available from Crompton (Geo Specialty Chemicals). Similar initiating agents are available from AkroChem, Lanxess, Flexsys/Harwick and R.T. Vanderbilt.

Another commercially-available and preferred initiating agent is TRIGONOX™ 265-508 from Akzo Nobel, which is a mixture of 1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane and di(2-t-butylperoxyisopropyl)benzene. TRIGONOX™ peroxides are generally sold on a carrier compound.

Suitable reactive co-agents include, but are not limited to, metal salts of dicarboxylic acids, dimethacrylates, and monomethacrylates suitable for use in this invention include those wherein the metal is zinc, magnesium, calcium, barium, tin, aluminum, lithium, sodium, potassium, iron, zinc, silicon, and bismuth. Zinc dicarboxylate (ZDA) is preferred, but the present invention is not limited thereto. ZDA provides golf balls with a high initial velocity. The ZDA can be of various grades of purity. For the purposes of this invention, the lower the quantity of zinc stearate present in the ZDA the higher the ZDA purity. ZDA containing less than about 10% zinc stearate is preferable. More preferable is ZDA containing about 4-8% zinc stearate. Suitable, commercially available zinc diacrylates include those from Cray Valley USA. The preferred concentrations of ZDA that can be used are about 10 phr to about 45 phr, more preferably 20 phr to about 40 phr, most preferably 25 phr to about 35 phr. In a particularly preferred embodiment, the reactive co-agent is present in an amount of about 29 phr to about 31 phr.

Additional preferred co-agents that may be used alone or in combination with those mentioned above include, but are not limited to, trimethylolpropane trimethacrylate, trimethylolpropane triacrylate, and the like. It is understood by those skilled in the art, that in the case where these co-
agents may be liquids at room temperature, it may be advantageous to disperse these compounds on a suitable carrier to promote ease of incorporation in the rubber mixture.

[0057] Antioxidants are compounds that inhibit or prevent the oxidative breakdown of elastomers, and/or inhibit or prevent reactions that are promoted by oxygen radicals. Some exemplary antioxidants that may be used in the present invention include, but are not limited to, quinoline type antioxidants, amine type antioxidants, and phenolic type antioxidants. A preferred antioxidant is 2,2'-methylene-bis-(4-methyl-6-t-butylphenol) available as VANOX® MBPC from R.T. Vanderbilt. Other polyphenolic antioxidants include VANOX® T, VANOX® I, VANOX® SKT, VANOX® SWP, VANOX® 13 and VANOX® 1290.

[0058] The antioxidant is typically present in an amount of about 0.1 phr to about 5 phr, preferably from about 0.1 phr to about 2 phr, more preferably about 0.1 phr to about 1 phr. In a particularly preferred embodiment, the antioxidant is present in an amount of about 0.4 phr. In an alternative embodiment, the antioxidant should be present in an amount to ensure that the hardness gradient of the inventive cores is negative. Preferably, about 0.2 phr to about 1 phr antioxidant is added to the core layer (center or outer core layer) formulation, more preferably, about 0.3 to about 0.8 phr, and most preferably about 0.4 to about 0.7 phr. Preferably, about 0.25 phr to about 1.5 phr of peroxide as calculated at 100% active can be added to the core formulation, more preferably about 0.5 phr to about 1.2 phr, and most preferably about 0.7 phr to about 1.0 phr. The ZDA amount can be varied to suit the desired compression, spin and feel of the resulting golf ball. The cure regime can have a temperature range between from about 290°F to about 365°F, more preferably about 325°F to about 350°F, and the stock is held at that temperature for at least about 10 minutes to about 30 minutes.

[0059] The thermostet rubber composition of the present invention may also include an optional soft and fast agent. As used herein, "soft and fast agent" means any compound or a blend thereof that is capable of making a core 1) be softer (lower compression) at constant Cor 2) have a higher Cor at equal compression, or any combination thereof, when compared to a core equivalently prepared without a soft and fast agent. Preferably, the composition of the present invention contains from about 0.05 phr to about 10.0 phr soft and fast agent. In one embodiment, the soft and fast agent is present in an amount of about 0.05 phr to about 3.0 phr, preferably about 0.1 phr to about 2.0 phr, more preferably about 0.15 phr to about 1.0 phr. In another embodiment, the soft and fast agent is present in an amount of about 2.0 phr to about 5.0 phr, preferably about 2.35 phr to about 4.0 phr, and more preferably about 2.35 phr to about 3.0 phr. In an alternative high concentration embodiment, the soft and fast agent is present in an amount of about 5.0 phr to about 10.0 phr, more preferably about 6.0 phr to about 9.0 phr, most preferably about 7.0 phr to about 8.0 phr. In a most preferred embodiment, the soft and fast agent is present in an amount of about 2.6 phr.

[0060] Suitable soft and fast agents include, but are not limited to, organosulfur or metal-containing organosulfur compounds, an organic sulfur compound, including mono, di, and polysulfides, a thiol, or mercaptan compound, an inorganic sulfide compound, a Group VIA compound, or mixtures thereof. The soft and fast agent component may also be a blend of an organosulfur compound and an inorganic sulfide compound.

Suitable soft and fast agents of the present invention include, but are not limited to those having the following general formula:

![Chemical Structure](image)

where R₁−R₅ can be C₁−C₆ alkyl groups; halogen groups; thiol groups (—SH), carboxylated groups; sulfonated groups; and hydrogen; in any order; and also pentfluorothiophenol; 2-fluorothiophenol; 3-fluorothiophenol; 4-fluorothiophenol; 2,3-fluorothiophenol; 2,4-fluorothiophenol; 3,4-fluorothiophenol; 3,5-fluorothiophenol; 2,3,4,5-tetrafluorothiophenol; 2,3,5,6-tetrafluorothiophenol; 4-chlorotetrafluorothiophenol; pentachlorothiophenol; 2-chlorothiophenol; 3-chlorothiophenol; 4-chlorothiophenol; 2,3-chlorothiophenol; 2,4-chlorothiophenol; 3,4-chlorothiophenol; 3,5-chlorothiophenol; 2,3,4,5-tetrachlorothiophenol; 2,3,5,6-tetrachlorothiophenol; pentabromothiophenol; 2-bromothiophenol; 3-bromothiophenol; 4-bromothiophenol; 2,3-bromothiophenol; 2,4-bromothiophenol; 3,4-bromothiophenol; 3,5-bromothiophenol; 2,3,4-bromothiophenol; 3,4,5-bromothiophenol; 2,3,4,5-tetrabromothiophenol; pentaoctothiophenol; 2-iodothiophenol; 3-iodothiophenol; 4-iodothiophenol; 3,4,5-iodothiophenol; 2,3,5,6-tetraiodothiophenol; and their zinc salts. Preferably, the halogenated thiophenol compound is pentachlorothiophenol, which is commercially available in neat form or under the tradename STRUKTOL® A95, a clay-based carrier containing the sulfur compound pentachlorothiophenol loaded at 45 percent. STRUKTOL® A95 is commercially available from Struktol Company of America of Stow, Ohio. PCTP is commercially available in neat form from eChinachem of San Francisco, Calif. and in the salt form from eChinachem of San Francisco, Calif. Most preferably, the halogenated thiophenol compound is the zinc salt of pentachlorothiophenol, which is commercially available from eChinachem of San Francisco, Calif.

[0061] As used herein when referring to the invention, the term “organosulfur compound(s)” refers to any compound containing carbon, hydrogen, and sulfur, where the sulfur is directly bonded to at least 1 carbon. As used herein, the term “sulfur compound” means a compound that is elemental sulfur, polymeric sulfur, or a combination thereof. It should be further understood that the term “elemental sulfur” refers to the ring structure of S₈ and that “polymeric sulfur” is a structure including at least one additional sulfur relative to elemental sulfur. Additional suitable examples of soft and fast agents (that are also believed to be cis-to-trans catalysts) include, but are not limited to, 4,4’-diphenyl disulfide; 4,4’-diphenyl disulfide; 2,2’-benzamide diphenyl disulfide; bis(2-aminophenyl)disulfide;
bis(4-aminophenyl)disulfide; bis(3-aminophenyl)disulfide; 2,2'-bis(4-aminophenyl)disulfide; 2,2'-bis(3-aminophenyl)disulfide; 2,2'-bis(4-aminonaphthyl)disulfide; 2,2'-bis(3-aminonaphthyl)disulfide; 1,1'-bis(2-aminophenyl)disulfide; 1,1'-bis(3-aminophenyl)disulfide; 1,1'-bis(3-aminonaphthyl)disulfide; 1,1'-bis(4-aminonaphthyl)disulfide; 1,1'-bis(5-aminonaphthyl)disulfide; 1,1'-bis(6-aminonaphthyl)disulfide; 1,1'-bis(7-aminonaphthyl)disulfide; 1,1'-bis(8-aminonaphthyl)disulfide; 1,2'-diamino-1,2'-dithiodiphenyl; 2,3'-diamino-1,2'-dithiodiphenyl; bis(4-chlorophenyl)disulfide; bis(2-chlorophenyl)disulfide; bis(3-chlorophenyl)disulfide; bis(4-bromophenyl)disulfide; bis(2-bromophenyl)disulfide; bis(3-bromophenyl)disulfide; bis(4-fluorophenyl)disulfide; bis(4-iodophenyl)disulfide; bis(2,5-dichlorophenyl)disulfide; bis(3,5-dichlorophenyl)disulfide; bis(2,4-dichlorophenyl)disulfide; bis(2,6-dichlorophenyl)disulfide; bis(2,5-dibromophenyl)disulfide; bis(3,5-dibromophenyl)disulfide; bis(2-chloro-5-bromophenyl)disulfide; bis(2,4,6-trichlorophenyl)disulfide; bis(2,3,4,5,6-pentachlorophenyl)disulfide; bis(4-cyanophenyl)disulfide; bis(2-cyanophenyl)disulfide; bis(4-nitrophenyl)disulfide; bis(2-nitrophenyl)disulfide; 2,2'-dithiobenzoic acid ethylester; 2,2'-dithiobenzoic acid methylster; 2,2'-dithiobenzoic acid ethylester; 4,4'-dithiobenzoic acid ethylester; bis(4-acetylphenyl)disulfide; bis(4-acetylphenyl)disulfide; bis(4-formylphenyl)disulfide; bis(4-carbamoylphenyl)disulfide; 1,1'-dinaphthyl disulfide; 2,2'-dinaphthyl disulfide; 1,1'-dinaphthyl disulfide; 2,2'-bis(1-chloronaphthyl)disulfide; 2,2'-bis(1-bromonaphthyl)disulfide; 1,1'-bis(2-chloronaphthyl)disulfide; 2,2'-bis(1-cyanonaphthyl)disulfide; 2,2'-bis(1-acetylphenyl)disulfide; and the like; or a mixture thereof. Preferred organosulfur components include 4,4'-diphenyl disulfide, 4,4'-diphenyl disulfide, or 2,2'-benzamido diphenyl disulfide, or a mixture thereof. A more preferred organosulfur component includes 4,4'-diphenyl disulfide. In another embodiment, metal-containing organosulfur components can be used according to the invention. Suitable metal-containing organosulfur components include, but are not limited to, cadmium, copper, lead, and tellurium analogs of diethylthiocarbamate, dimethylthiocarbamate, or mixtures thereof.

[0062] Suitable substituted or unsubstituted aromatic organic components that do not include sulfur or a metal include, but are not limited to, 4,4'-diphenyl acetylene, azobenzene, or a mixture thereof. The aromatic organic group preferably ranges in size from C₆ to C₂₀, and more preferably from C₆ to C₁₀. Suitable inorganic sulfide components include, but are not limited to, titanium sulfide, manganese sulfide, and sulfide analogs of iron, calcium, cobalt, molybdenum, tungsten, copper, selenium, yttrium, zinc, tin, and bismuth.

[0063] A substituted or unsubstituted aromatic organic compound is also suitable as a soft and fast agent. Suitable substituted or unsubstituted aromatic organic components include, but are not limited to, components having the formula \( (R₁)ₙ - R₂-M-R₃ \), wherein \( R₁ \) and \( R₂ \) are each hydrogen or a substituted or unsubstituted \( C₁-C₂₀ \) linear, branched, or cyclic alkyl, alkoxy, or alkylthio group, or a single, multiple, or fused ring \( C₅ \) to \( C₂₄ \) aromatic group; and \( M \) includes an azo group or a metal component. \( R₃ \) and \( R₄ \) are each preferably selected from phenyl, benzyl, naphthyl, benzimidazo, and benzothiazyl. \( R₄ \) and \( R₅ \) are each preferably selected from a substituted or unsubstituted \( C₁-C₁₀ \) linear, branched, or cyclic alkyl, alkoxy, or alkylthio group or a \( C₆ \) to \( C₁₀ \) aromatic group. When \( R₄ \), \( R₅ \), \( R₆ \), or \( R₇ \) are substituted, the substitution may include one or more of the following substituent groups: hydroxy and metal salts thereof; mercapto and metal salts thereof; halogen; amino, nitro, cyano, and amido; carbonyl including esters, acids, and metal salts thereof; silyl; acrylates and metal salts thereof; sulfonyl or sulfonamide; and phosphates and phosphites. When \( M \) is a metal component, it may be any suitable element metal available to those of ordinary skill in the art. Typically, the metal will be a transition metal, although preferably it is tellurium or selenium. In one embodiment, the aromatic organic compound is substantially free of metal, while in another embodiment the aromatic organic compound is completely free of metal.

[0064] The soft and fast agent can also include a Group VIA component. Elemental sulfur and polymeric sulfur are commercially available from Elastochem, Inc. of Chardon, Ohio. Exemplary sulfur catalyst compounds include PP(RM-S)-80 elemental sulfur and PP(CRST)-65 polymeric sulfur, each of which is available from Elastochem, Inc. An exemplary tellurium catalyst under the tradename TELLLOY® and an exemplary selenium catalyst under the tradename VANDEX® are each commercially available from RT Vanderbilt.

[0065] Other suitable soft and fast agents include, but are not limited to, hydroquinones, benzoquinones, quinhydrones, catechols, and resorcins.

[0066] Fillers may also be added to the thermoset rubber composition of the core to adjust the density of the composition, up or down. Typically, fillers include materials such as tungsten, zinc oxide, barium sulfate, silica, calcium carbonate, zinc carbonate, metals, metal oxides and salts, regrind (recycled core material typically ground to about 30 mesh particle), high-Mooney-viscosity rubber regrind, trans-re grind core material (recycled core material containing high trans-isomer of polybutadiene), and the like. When transregrind is present, the amount of trans-isomer is preferably between about 10% and about 60%. In a preferred embodiment of the invention, the core comprises polybutadiene having a cis-isomer content of greater than about 95% and trans-regrind core material (already Vulcanized) as a filler.

[0067] Fillers added to one or more portions of the golf ball typically include processing aids or compounds to affect rheological and mixing properties, density-modifying fillers, tear strength, or reinforcement fillers, and the like. The fillers are generally inorganic, and suitable fillers include numerous metals or metal oxides, such as zinc oxide and tin oxide, as well as barium sulfate, zinc sulfate, calcium carbonate, barium carbonate, clay, tungsten, tungsten carbide, an array of silicas, and mixtures thereof. Fillers may also include various foaming agents or blowing agents which may be readily selected by one of ordinary skill in the art. Fillers may include polymeric, ceramic, metal, and glass microspheres may be solid or hollow, and filled or unfilled. Fillers are typically also added to one or more portions of the golf ball to modify the density thereof to conform to uniform golf ball standards. Fillers may also be used to modify the weight of the center or at least one additional layer.
The polybutadiene and/or any other base rubber or elastomer system may also be foamed, or filled with hollow microspheres or with expandable microspheres which expand at a set temperature during the curing process to any low specific gravity level. Other ingredients such as sulfur accelerators, e.g., tetra methylthiurium di, tri, or tetrathiole, and/or metal-containing organosulfur components may also be used according to the invention. Suitable metal-containing organosulfur accelerators include, but are not limited to, cadmium, copper, lead, and tellurium analogs of diethylthiocarbamate, dianyldithiocarbamate, and dimethylthiocarbamate, or mixtures thereof. Other ingredients such as processing aids e.g., fatty acids and/or their metal salts, processing oils, dyes and pigments, as well as other additives known to one skilled in the art may also be used in the present invention in amounts sufficient to achieve the purpose for which they are typically used.

Any cover material listed herein would be suitable and an inner cover may or may not be present. Preferably, an inner cover layer is present and it is an ionomer-based material, such as a highly-neutralized ionomer or a blend of high-acid ionomers and FUSABOND®. Preferably the outer cover is formed from a castable urethane or urea material.

While the inventive golf ball may be formed from a variety of differing and conventional cover materials (both intermediate layer(s) and outer cover layer(s)), preferred cover materials include, but are not limited to:

1. Polyurethanes, such as those prepared from polyols or polyamines and disocyanates or polyisocyanates and/or their prepolymers, and those disclosed in U.S. Pat. Nos. 5,334,673 and 6,506,851;
2. Polyureas, such as those disclosed in U.S. Pat. Nos. 5,484,870 and 6,835,794; and
3. Polyurethane-urea hybrids, blends or copolymers comprising urethane or urea segments.

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. Pat. No. 7,331,878, which is incorporated herein in its entirety by reference.

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'-diisocyanatetethyl methacrylate (MDI); polymeric MDI; carbodiimide-modified liquid MDI; 4,4'-dicyclohexylmethane diisocyanate (H₂MDI); p-phenylene diisocyanate (PPDI); m-phenylene diisocyanate (MPDI); toluene diisocyanate (TDI); 3,3'-dimethyl-1,4'-biphenylene diisocyanate; isophoronediisocyanate; 1,6-hexamethylene diisocyanate (HDI); tolylene diisocyanate; xylene diisocyanate; and tetramethylylene diisocyanate; m-tetramethylylene diisocyanate; ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; cyclohexyl diisocyanate; dodecan-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-5,5,5-trimethyl-1-isocyanatomethylcyclohexane; methyl cyclohexylene diisocyanate; trisocyanate of HDI; trisocyanate 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 and, additionally, that the diisocyanate employed may be “low free monomer,” understood by one of ordinary skill in the art to have lower levels of “free” monomer isocyanate groups, typically less than about 0.1% free monomer isocyanate groups. Examples of “low free monomer” diisocyanates include, but are not limited to Low Free Monomer MDI, Low Free Monomer TDI, and Low Free Monomer PPDI.

The at least one polyisocyanate should have less than about 14% unreacted NCO groups. Preferably, the at least one polyisocyanate has no greater than about 8.0% NCO, preferably no greater than about 7.8%, and most preferably no greater than about 7.5% NCO with a level of NCO of about 7.2 or 7 or, 6.5% NCO commonly used.

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, polyoxypolyethylene 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.

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-phthalic-1,6-hexanediol; poly(hexamethylenediamine) adipate glycol; and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

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

In yet another embodiment, polycarbonate polyols are included in the polyurethane material of the invention. Suitable polycarbonates include, but are not limited to, polyphthallic carbonate and poly(hexamethylenecarbonate) glycol. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.
cyclic groups. In one embodiment, the molecular weight of the polyol is from about 200 to about 4000. 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-dimethyl-2,4,6-trihydroxyaniline and isomers thereof; 3,5-diethylhexyl-2,4-diamine and isomers thereof, such as 3,5-dihydroxybenzene-2,4-diamine; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroanilnine); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkylamino diphenylmethane; p,p'-methylene diamline; m-phenylenediamine; 4,4'-methylene-bis-(2-chloroanilnine); 4,4'-methylene-bis-(2,6-diethylaniline); 4,4'-methylene-bis-(2,3-dichloroanilnine); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diaminodiphenylmethane; trimethylene glycol di-p-aminobenzoate; and mixtures thereof. Preferably, the curing agent of the present invention includes 3,5-dimethyl-2,4,6-trihydroxyaniline and isomers thereof, such as ETHACURE® 300, commercially available from Albemarle 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.

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; and 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-hydroxyethoxy)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-hydroxyethoxy)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.

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.

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 thermostet and thermoplastic polyurethanes.

In this embodiment, the saturated polyurethanes of the present invention are substantially free of aromatic groups or moieties. Saturated polyurethanes suitable for use in the invention are a product of a reaction between at least one polyurethane prepolymer and at least one saturated curing agent. The polyurethane prepolymers are a product formed by a reaction between at least one saturated polyol and at least one saturated disocyanate. As is well known in the art, that a catalyst may be employed to promote the reaction between the curing agent and the isocyanate and polyol, or the curing agent and the prepolymers.

Saturated disocyanates which can be used include, without limitation, ethylene disocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-disocyanate; 1,6-hexamethylene-disocyanate (HDI); 2,2,4-trimethylhexamethylene disocyanate; 2,4,4-trimethylhexamethylene disocyanate; dodecane-1,12-diisocyanate; diclohexyloxy methane disocyanate; cyclobutane-1,3-disocyanate; cyclohexane-1,3-disocyanate; cyclohexane-1,4-disocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-1-cyclohexane; isophorone disocyanate; methyl cyclohexylene disocyanate; triisocyanate of HDI; trisocyanate of 2,2,4-trimethyl-1,6-hexane disocyanate. The most well-recognized saturated disocyanates are 4,4'-dicyclohexyloxy methane disocyanate and isophorone disocyanate.

Saturated polyols which are appropriate for use in this invention include without limitation polyether polyols such as polytetramethylene ether glycol and poly(oxypropylene) glycol. Suitable saturated polyester polyols include polyethylene adipate glycol, polyethylene propylene adipate glycol, polybutylene adipate glycol, polycarbonate polyol and ethylene oxide-capped polyoxypropylene diols. Saturated polycaprolactone polyols which are useful in the invention include diethylene glycol-initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, 1,6-hexanediol-initiated polycaprolactone, trimethylol propane-initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, and polytetramethylene ether glycol-initiated polycaprolactone. The most preferred saturated polyols are polyltetramethylene ether glycol and PTMEG-initiated polycaprolactone.

Suitable saturated curatives include 1,4-butanediol, ethylene glycol, diethylene glycol, polytetramethylene ether glycol, propylene glycol; trimethanolpropane; tetra-(2-hydroxypropyl)-ethylenediamine; and isomers and mixtures of isomers of cyclohexylmethy1ol, isomers and mixtures of isomers of cyclohexane bis(methylene); tris(propoxyl)amine; ethylene diamine; diethylene triamine; triethylene tetramine; tetraethylene pentamine; 4,4'-dicyclohexylmethane diamine; 2,2,4,4'-trimethyl-1,6-hexanediame; 2,4,4'-trimethyl-1,6-hexanediame; diethylene glycol di-(aminopropyl)ether; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,2-bis-(sec-butylamino)cyclohexane; 1,4-bis-(sec-butylamino) cyclohexane; isophorone diamine; hexamethylene diamine; propylene diamine; 1-methyl-2,4-cyclohexyl diamine; 1-methyl-1,2,6-cyclohexyl diamine; 1,3-diaminopropane; dimethylamine propylene diamine; diethylenamine propylene diamine; imido-bis-propylene diamine; isomers and mixtures of isomers of diaminocyclohexane; monoethanolamine; diethanolamine; triethanolamine; monoisopropanolamine; and disopropanolamine. The most preferred saturated curatives are 1,4-butanediol, 1,4-cyclohexyldimethyl and 4,4'-bis-(sec-butylamino)-dicyclohexylmethane.

Alternatively, other suitable polymers include partially or fully neutralized ionomer, metalloocene, 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. Thermosetting polyurethanes or polyureas are suitable for the outer cover layers of the golf balls of the present invention. Additionally, polyurethane can be replaced with or blended with a polyurea material. Polyureas are distinctly different from polyurethane compositions, but also result in desirable aerodynamic and aesthetic characteristics when used in golf ball components. The polyurea-based compositions are preferably saturated in nature.

Without being bound to any particular theory, it is now believed that substitution of the long chain polyol segment in the polyurethane prepolymer with a long chain polyamine oligomer soft segment to form a polyurea prepolymer, improves shear, cut, and resiliency, as well as adhesion to other components. Thus, the polyurea compositions of this invention may be formed from the reaction product of an isocyanate and polyamine prepolymer crosslinked with a curing agent. For example, polyurea-based compositions of the invention may be prepared from at least one isocyanate, at least one polyether amine, and at least one diol curing agent or at least one diamine curing agent.

Any polyanion available to one of ordinary skill in the art is suitable for use in the polyurea prepolymer. Polyether amines are particularly suitable for use in the prepolymer. As used herein, "polyether amines" refer to at least poloxamolyleneamines containing primary amino groups attached to the terminus of a polyether backbone. Due to the rapid reactivity of isocyanate and amine, and the insolubility of many urea products, however, the selection of diaminos and polyether amines is limited to those allowing the successful formation of the polyurea prepolymer. In one embodiment, the polyether backbone is based on tetramethylene, propylene, ethylene, trimethylolpropane, glycerin, and mixtures thereof.

Suitable polyether amines include, but are not limited to, methylhexahedranolamine; polyevalylenediamines such as, polytetramethylene ether diamines, polyoxypropylenetriamine, and polyoxypropylene diamines; poly(ethylenoxide capped oxypropylene) ether diamines; propylene oxide-based triamines; triethyleneglycoldiamines; trimethylolpropane-based triaminos; glycerin-based triaminos; and mixtures thereof. In one embodiment, the polyether amine used to form the prepolymer is JEFFAMINE® D2000 (manufactured by Huntsman Chemical Co. of Austin, Tex.).

The molecular weight of the polyether amine for use in the polyurea prepolymer may range from about 100 to about 5000. In one embodiment, the polyether amine molecular weight is about 200 or greater, preferably about 230 or greater. In another embodiment, the molecular weight of the polyether amine is about 4000 or less. In yet another embodiment, the molecular weight of the polyether amine is about 600 or greater. In still another embodiment, the molecular weight of the polyether amine is about 3000 or less. In yet another embodiment, the molecular weight of the polyether amine is between about 1000 and about 3000, and more preferably is between about 1500 to about 2500. Because lower molecular weight polyether amines may be prone to forming solid polyureas, a higher molecular weight oligomer, such as JEFFAMINE® D2000, is preferred.

As briefly discussed above, some amines may be unsuitable for reaction with the isocyanate because of the rapid reaction between the two components. In particular, shorter chain amines are fast reacting. In one embodiment, however, a hindered secondary diamine may be suitable for use in the prepolymer. Without being bound to any particular theory, it is believed that an amine with a high level of steric hindrance, e.g., a tertiary butyl group on the nitrogen atom, has a slower reaction rate than an amine with no hindrance or a low level of hindrance. For example, 4,4'-bis(2-butylamino)-dicyclohexylmethane (CLEARLINK® 1000) may be suitable for use in combination with an isocyanate to form the polyurea prepolymer.

Any isocyanate available to one of ordinary skill in the art is suitable for use in the polyurea prepolymer. Isooctanates for use with the present invention include aliphatic, cycloaliphatic, arylaliphatic, aromatic, any derivatives thereof, and combinations of these compounds having two or more isocyanate (NCO) groups per molecule. The isocyanates may be organic polyisocyanate-terminated prepolymer. The isocyanate-containing reactable component may also include any isocyanate-functional monomer, dimer, trimmer, or multimeric adduct thereof, prepolymer, quasi-prepolymer, or mixtures thereof. Isooctanate-functional compounds may include monoisocyanates or polyisocyanates that include any isocyanate functionality of two or more.

Suitable isocyanate-containing components include disiocyanates having the generic structure: O═C—N—R—N═C—O, where R is preferably a cyclic, aromatic, or linear or branched hydrocarbon moiety containing from about 1 to about 20 carbon atoms. The disiocyanate may also contain one or more cyclic groups or one or more phenyl groups. When multiple cyclic or aromatic groups are present, linear and/or branched hydrocarbons containing from about 1 to about 10 carbon atoms can be present as spacers between the cyclic or aromatic groups. In some cases, the cyclic or aromatic group(s) may be substituted at the 2-, 3-, and/or 4-positions, or at the ortho-, meta-, and/or para-positions, respectively. Substituted groups may include, but are not limited to, halogens, primary, secondary, tertiary hydrocarbon groups, or a mixture thereof.

Examples of disiocyanates that can be used with the present invention include, but are not limited to, substituted and isocyanic mixtures including 2,2', 2,4'- and 2,4'-diphenylmethane diisocyanate; 3,3'-dimethyl-4,4'-biphenylene disiocyanate; toluene diisocyanate; polymeric MDI; carbodiimide-modified liquid 4,4'-diphenylmethane disiocyanate; para-phenylene diisocyanate; meta-phenylene diisocyanate; triphenyl methane-4,4'- and triphenyl methane-4,4'-trisocyanate; naphthylene-1,5-diisocyanate; 2,4', 4,4', and 2,2-biphenyl diisocyanate; polyphenyl polyisocyanate; mixtures of MDI and PMDI; mixtures of PMDI and TDI; ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,2-diisocyanate; tetramethylene-1,3-diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylenediisocyanate; octamethylene diisocyanate; decamethylene disiocyanate; 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,2-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; methylcyclohexylene diisocyanate; 2,4-methylcyclohexane diisocyanate; 2,6-methylcyclohexane diisocyanate; 4,4'-dicyclohexyl disiocyanate; 2,4'-dicyclohexyl diisocyanate; 1,3,5-cyclohexane trisocyanate; isoxyanatomethycyclohexane isocyanate; 1-isocyanato-3,3,5-trimethyl-5-isoxyanatomethycyclohexane; isoxyanatomethycyclohexane isocyanate; bis(isocyanatomethyl)-cyclohexane disiocyanate; 4,4'-bis(isocyanatomethyl) dicyclohexane; 2,4'-bis(isocyanatomethyl)dicyclohexane;
isophorone diisocyanate; triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate; 4,4'-dicyclohexylmethane diisocyanate; 2,4-hexahydrotoluene diisocyanate; 2,6-hexahydrotoluene diisocyanate; 1,2-, 1,3-, and 1,4-phenylene diisocyanate; aromatic aliphatic isocyanate, such as 1,2-, 1,3-, and 1,4-xylene diisocyanate; meta-tetramethylenediisocyanate; para-tetramethylenediisocyanate; trimerized isocyanurate of any polyisocyanate, such as isocyanurate of toluene diisocyanate, trimer of diphenylmethane diisocyanate, isocyanurate of hexamethylene diisocyanate, isocyanurate of isophorone diisocyanate, and mixtures thereof; dimerized ureidone of any polyisocyanate, such as uretdione of toluene diisocyanate, uretdione of hexamethylene diisocyanate, and mixtures thereof; modified polyisocyanate derived from the above isocyanates and polyisocyanates; and mixtures thereof.

Examples of saturated diisocyanates that can be used with the present invention include, but are not limited to, ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene diisocyanate; octamethylene diisocyanate; decamethylene diisocyanate; 2,2,4,4'-trimethylhexamethylene diisocyanate; 2,4,4'-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,2-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; methyl-cyclohexylene diisocyanate; 2,4-methylcyclohexylcyclohexene diisocyanate; 2,6-methylcyclohexylcyclohexene diisocyanate; 4,4'-dicyclohexyl diisocyanate; 2,4'-dicyclohexyl diisocyanate; 1,3,5-cyclohexane triisocyanate; isocyanatomethylcyclohexane isocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isocyanatoethylcyclohexene isocyanate; bis(isocyanatomethyl)-cyclohexene diisocyanate; 4,4'-bis(isocyanatomethyl)cyclohexane; 2,4'-bis(isocyanatomethyl) dicyclohexane; isophorone diisocyanate; triisocyanate of HDI; triisocyanate of 2,2,4,2'-trimethyl-1,6-hexane diisocyanate; 4,4'-dicyclohexylmethane diisocyanate; 2,4-hexahydrotoluene diisocyanate; 2,6-hexahydrotoluene diisocyanate; and mixtures thereof. Aromatic aliphatic isocyanates may also be used to form light stable materials. Examples of such isocyanates include 1,2-, 1,3-, and 1,4-xylene diisocyanate; meta-tetramethylenediisocyanate; para-tetramethylenediisocyanate; trimerized isocyanurate of any polyisocyanate, such as isocyanurate of toluene diisocyanate, trimer of diphenylmethane diisocyanate, trimer of tetramethylenediisocyanate, isocyanurate of hexamethylene diisocyanate, isocyanurate of isophorone diisocyanate, isocyanurate of isophorone diisocyanate, and mixtures thereof; dimerized ureidone of any polyisocyanate, such as uretdione of toluene diisocyanate, uretdione of hexamethylene diisocyanate, and mixtures thereof; modified polyisocyanate derived from the above isocyanates and polyisocyanates; and mixtures thereof. In addition, the aromatic aliphatic isocyanates may be mixed with any of the saturated isocyanates listed above for the purposes of this invention.

The number of unreacted NCO groups in the polyurea prepolymer of isocyanate and polyether amine may be varied to control such factors as the speed of the reaction, the resultant hardness of the composition, and the like. For instance, the number of unreacted NCO groups in the polyurea prepolymer of isocyanate and polyether amine may be less than about 14 percent. In one embodiment, the polyurea prepolymer has from about 5 percent to about 11 percent unreacted NCO groups, and even more preferably has from about 6 to about 9.5 percent unreacted NCO groups. In one embodiment, the percentage of unreacted NCO groups is about 3 percent to about 9 percent. Alternatively, the percentage of unreacted NCO groups in the polyurea prepolymer may be about 7.5 percent or less, and more preferably, about 7 percent or less. In another embodiment, the unreacted NCO content is from about 2.5 percent to about 7.5 percent, and more preferably from about 4 percent to about 6.5 percent.

When formed, polyurea prepolymers may contain about 10 percent to about 20 percent by weight of the prepolymer of free isocyanate monomer. Thus, in one embodiment, the polyurea prepolymer may be stripped of the free isocyanate monomer. For example, after stripping, the prepolymer may contain about 1 percent or less free isocyanate monomer. In another embodiment, the prepolymer contains about 0.5 percent by weight or less of free isocyanate monomer.

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 polyols 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.

The polyurea composition can be formed by crosslinking the 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.

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-(methylene); 1,3-cyclohexane-bis-(methylene); diethyleneglycol di-(aminopropyl) ether; 2-methylpentamethylene diamine; dianioncyclohexane; diethylenetriamine; triethylenetetramine; tetraethylenepentamine; propylene diamine; 1,3-diaminopropene; dimethylaminopropylamine; diethylaminopropylamine; dipropylene triamine; imido-bispropylamine; monoethanolamine, diethanolamine; triethanolamine; monoisopropanolamine, diisopropanolamine; isophoronediamine; 4,4'-methylenebis-(2-chloroaniline); 3,5; dimethylthio-2,4-toluenediamine; 5,5-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',N'-diallylamino-diphenylmethane; N,N,N',N'-tetraakis(2-hydroxypropyl)ethylene diamine; trimethylenglycol-di-p-aminoenzout; polytetramethyleneoxide-di-p-aminoenzout; 4,4'-methylenebis-(3-chloro-2,6-diethylenecotinine); 4,4'-methylenebis-(2,6-diethyleneliane); meta-phenylenediamine; paraphenylene diamine; and mixtures thereof. In one embodiment, the amine-terminated curing agent is 4,4'-bis-(sec-butylamino)-dicyclohexylmethane.

[0101] 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-hexamethine diamine; 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-diethylenemacrocyclohexane; 1,4-cyclohexane-bis (methylene); 1,3-cyclohexane-bis (methylene); diethylene glycol di-(aminopropyl) ether; 2-methylpentamethylene diamine; diamino cyclohexane; diethylene triamine; triethylenetetramine; tetraethylenepentamine; propylene diamine; 1,3-diaminobutane; dimethylaminopropylamine; diethylenimine propylene diamine; imidobis-propylene diamine; monoethanolamine, diethanolamine, triethanolamine; mono- propylene amine; diisopropylamine; isophoronediamine; triisopropanolamine; and mixtures thereof. In addition, any of the polyether amine listed above may be used as curing agents to react with the polyurea prepolymers.

[0102] Core or inner over layers of the inventive golf ball may also be formed from ionomer polymer, preferably highly-neutralized ionomers (HNPs). 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 also be blended with a second polymer component, which, if containing an acid group, may be neutralized in a conventional manner, by the organic fatty acids of the present invention, or both. The second polymer component, which may be partially or fully neutralized, preferably comprises ionomer copolymers and terpolymers, ionomer precursors, thermoplastics, polyamides, polycarbonates, polyesters, polyurethanes, polyureas, thermoplastic elastomers, polybutadiene rubber, balata, metalloocene-catalyzed polymers (grafted and non-rafted), 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 about 3000 psi and about 200,000 psi.

[0103] In one embodiment of the present invention the HNPs 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 α-olefins, such as ethylene, C3, C5 α-olefins and ethylene/α-olefin 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.

[0104] The acid copolymers can be described as E/X/Y copolymers where E is ethylene, X is an α,β-ethylenically unsaturated carboxylic acid, and Y is a softening comonomer. In a preferred embodiment, X is acrylic or methacrylic acid and Y is a C1-8 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.

[0105] 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/isobutyl acrylate, ethylene/acrylic acid/isobutyl acrylate, ethylene/methacrylic acid/n-butyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacrylate. Preferred acid-containing ethylene copolymers include, ethylene/methacrylic acid/n-butyl acrylate, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacrylate. The 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.

[0106] 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, however, 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 accomplished by melt-blending an ethylene α,β-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%.

[0107] 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).

[0108] 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.

[0109] Another preferred cover material in the two-piece embodiment is a thermoplastic or thermosetting polyurethane or polyurea.

[0110] A preferred ionomer is a high acid ionomer comprising a copolymer of ethylene and methacrylic or acrylic acid and having an acid content of at least 16 to about 25 weight percent.

[0111] A cover material may also comprise a castable or reaction injection moldable polyurethane, polyurea, or copolymer or hybrid of polyurethane/polyurea. Preferably, this cover is thermosetting but may be a thermoplastic, having a Shore D hardness of about 20 to about 70, more preferably about 30 to about 65 and more preferably about 35 to about 60. A moisture vapor barrier layer, such as disclosed in U.S. Pat. Nos. 6,632,147; 6,932,720; 7,044,854; and 7,182,702, all of which are incorporated by reference herein in their entirety, are optionally employed between the cover layer and the core.

[0112] 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 330 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). Most preferably the number of dimples is 330, 332, or 392 and comprises 5 to 7 dimples sizes and the parting line is a SWPL.

[0113] 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. 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.

[0114] Notwithstanding that the numerical ranges and parameters set 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 contain 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. While it is apparent that the illustrative embodiments of the invention disclosed herein fulfill the objective stated above, it is appreciated that numerous modifications and other embodiments may be devised by those skilled in the art. 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.

What is claimed is:

1. A golf ball comprising a core, a cover, and a casing layer disposed between the core and the cover; wherein the core has a first outer surface and a geometric center;

the geometric center having a hardness X of from about 40 Shore C to about 75 Shore C and the first outer surface having a hardness Y of from about 75 Shore C to about 95 Shore C such that (15 Shore C-Ψ(X-Ψ))≤(55 Shore C); and

wherein the casing layer is formed from a high acid divalent ionomeric composition and has an inner surface that is adjacent the first outer surface and a second outer surface surrounding the inner surface;

the second outer surface having a hardness Z of from about 90 Shore C to about 100 Shore C;

wherein (20 Shore C-Ψ(Z-Ψ))≤(60 Shore C); and wherein the core has an Atti compression A of from about 40 to about 100, and wherein the core and the casing layer, combined, have an Atti compression B of from about 55 to about 115 such that 1.05≤(8(A)A)≤1.75; and wherein the finished golf ball has an Atti compression of from about 60 to about 120.

2. The golf ball of claim 1, wherein the high acid divalent ionomeric composition is blended with a filler selected from the group consisting of fibers, flocks, flakes, glass flakes, microballoons, glass fibers, polymeric fiber, polymeric floc, silica and clay.

3. The golf ball of claim 1, wherein the high acid divalent ionomeric composition is partially neutralized with a divalent cation selected from the group consisting of zinc, magnesium, calcium, and blends thereof.

4. The golf ball of claim 1, wherein the high acid divalent ionomeric composition is an ethylene/methacrylic acid (E/MAA) copolymer having 19% methacrylic acid.

5. The golf ball of claim 1, wherein the cover has a cover inner surface adjacent the casing layer and a cover outer surface surrounding the cover inner surface, wherein the cover outer surface has a hardness Q of from about 70 Shore C to about 95 Shore C and wherein Q≤Z.

6. The golf ball of claim 1, wherein hardness X is from about 45 Shore C to about 70 Shore C, Y is from about 77 Shore C to about 86 Shore C and Z is from about 90 Shore C to about 94 Shore C.

7. The golf ball of claim 5, wherein hardness Q is from about 75 Shore C to about 94 Shore C.

8. The golf ball of claim 1, wherein hardness X is from about 55 Shore C to about 74 Shore C, Y is from about 81 Shore C to about 90 Shore C and Z is from about 93 Shore C to about 96 Shore C.

9. The golf ball of claim 5, wherein hardness Q is from about 80 Shore C to about 95 Shore C.

10. The golf ball of claim 1, wherein hardness X is from about 65 Shore C to about 68 Shore C, Y is from about 84 Shore C to about 89 Shore C and Z is from about 97 Shore C to about 99 Shore C.

11. The golf ball of claim 5, wherein hardness Q is from about 85 Shore C to about 95 Shore C.

12. A golf ball comprising a core, a cover, and a casing layer disposed between the core and the cover, wherein the core has a first outer surface and a geometric center;
the geometric center having a hardness X' of from about 15 Shore D to about 54 Shore D and the first outer surface having a hardness Y' of from about 35 Shore D to about 65 Shore D such that (10 Shore D)\(-(Y'\sim X')\) is (35 Shore D); and

wherein the casing layer is formed from a high acid divalent ionomeric composition and has an inner surface that is adjacent the first outer surface and a second outer surface surrounding the inner surface;

the second outer surface having a hardness Z' of from about 60 Shore D to about 75 Shore D;

wherein (10 Shore D)\-(Z'\sim X') is (55 Shore D); and

wherein the core has an Atti compression A of from about 40 to about 100, and wherein the core and the casing layer, combined, have an Atti compression B of from about 55 to about 115 such that 1.05B/A \sim 1.75; and wherein the finished golf ball has an Atti compression of from about 60 to about 120.

13. The golf ball of claim 12, wherein the high acid divalent ionomeric composition is blended with a filler selected from the group consisting of fibers, flocks, flakes, glass flakes, microballoons, glass fibers, polymeric fiber, polymeric flock, silica, clay, and combinations thereof.

14. The golf ball of claim 12, wherein the high acid divalent ionomeric composition is neutralized with a divalent cation selected from the group consisting of zinc, magnesium, calcium, and blends thereof.

15. The golf ball of claim 12, wherein the high acid divalent ionomeric composition is an ethylene/methacrylic acid (E/MAA) copolymer having 19% methacrylic acid.

16. The golf ball of claim 12, wherein the cover has a cover inner surface adjacent the casing layer and a cover outer surface surrounding the cover inner surface, wherein the cover outer surface has a hardness Q of from about 50 Shore D to about 68 Shore D and wherein Q' \sim Z'.

17. The golf ball of claim 16, wherein hardness X' is from about 20 Shore D to about 45 Shore D, Y' is from about 35 Shore D to about 56 Shore D and Z' is from about 62 Shore D to about 73 Shore D.

18. The golf ball of claim 17, wherein hardness Q' is from about 50 Shore D to about 65 Shore D.

19. The golf ball of claim 16, wherein hardness X' is from about 30 Shore D to about 40 Shore D, Y' is from about 41 Shore D to about 54 Shore D and Z' is from about 65 Shore D to about 71 Shore D.

20. The golf ball of claim 19, wherein hardness Q' is from about 55 Shore D to about 65 Shore D.

21. The golf ball of claim 12, wherein hardness X' is from about 35 Shore D to about 38 Shore D, Y' is from about 48 Shore D to about 50 Shore D and Z' is from about 68 Shore D to about 73 Shore D.

22. The golf ball of claim 16, wherein hardness Q' is from about 60 Shore D to about 65 Shore D.

23. A method of making a golf ball comprising:

providing a core;

wherein the core has a first outer surface and a geometric center; the geometric center having a hardness X of from about 40 Shore C to about 75 Shore C and the first outer surface having a hardness Y of from about 75 Shore C to about 95 Shore C such that (15 Shore C)-(Y\sim X') is (55 Shore C); and

wherein the core has an Atti compression A of from about 40 to about 100;

forming a casing layer about the core;

wherein the casing layer is formed from a high acid divalent ionomeric composition and has an inner surface that is adjacent the first outer surface and a second outer surface surrounding the inner surface; the second outer surface having a hardness Z of from about 90 Shore C to about 100 Shore C;

wherein (20 Shore C)-(Z\sim X') is (60 Shore C); and

wherein the core and the casing layer, combined, have an Atti compression B of from about 55 to about 115 such that 1.05B/A \sim 1.75; and

forming a cover about the casing layer such that the finished golf ball has an Atti compression of from about 60 to about 120.

24. The method of claim 23, wherein the high acid divalent ionomeric composition is blended with a filler selected from the group consisting of fibers, flocks, flakes, glass flakes, microballoons, glass fibers, polymeric fiber, polymeric flock, silica, clay, and combinations thereof.

25. The method of claim 23, wherein the high acid divalent ionomeric composition is neutralized with a divalent cation selected from the group consisting of zinc, magnesium and calcium.

26. The golf ball of claim 23, wherein the high acid divalent ionomeric composition is an ethylene/methacrylic acid (E/MAA) copolymer having 19% methacrylic acid.

27. The method of claim 23, wherein the cover has a cover inner surface adjacent the casing layer and a cover outer surface surrounding the cover inner surface, wherein the cover outer surface has a hardness Q of from about 70 Shore C to about 95 Shore C and wherein Q\sim Z.

28. The method of claim 23, wherein hardness X is from about 45 Shore C to about 70 Shore C, Y is from about 77 Shore C to about 86 Shore C and Z is from about 90 Shore C to about 94 Shore C.

29. The method of claim 27, wherein hardness Q is from about 75 Shore C to about 94 Shore C.

30. The method of claim 23, wherein hardness X is from about 55 Shore C to about 74 Shore C, Y is from about 81 Shore C to about 90 Shore C and Z is from about 93 Shore C to about 96 Shore C.

31. The method of claim 27, wherein hardness Q is from about 80 Shore C to about 95 Shore C.

32. The method of claim 23, wherein hardness X is from about 65 Shore C to about 68 Shore C, Y is from about 84 Shore C to about 89 Shore C and Z is from about 97 Shore C to about 99 Shore C.

33. The method of claim 27, wherein hardness Q is from about 85 Shore C to about 95 Shore C.

34. A method of making a golf ball comprising:

providing a core;

wherein the core has a first outer surface and a geometric center; the geometric center having a hardness X' of from about 15 Shore D to about 54 Shore D and the first outer surface having a hardness Y' of from about 35 Shore D to about 65 Shore D such that (10 Shore D)-(Y'\sim X') is (35 Shore D); and

wherein the core has an Atti compression A of from about 40 to about 100;

forming a casing layer about the core;

wherein the casing layer is formed from a high acid divalent ionomeric composition and has an inner surface that is adjacent the first outer surface and a second outer surface surrounding the inner surface; the second outer surface having a hardness Z of from about 90 Shore C to about 100 Shore C;

wherein (20 Shore C)-(Z\sim X') is (60 Shore C); and

wherein the core and the casing layer, combined, have an Atti compression B of from about 55 to about 115 such that 1.05B/A \sim 1.75; and

forming a cover about the casing layer such that the finished golf ball has an Atti compression of from about 60 to about 120.
second outer surface having a hardness $Z'$ of from
about 60 Shore D to about 75 Shore D;
wherein (10 Shore D) < $(Z' - X') < (55 Shore D)$; and
wherein the core and the casing layer, combined, have an
Attini compression B of from about 55 to about 115;
such that $1.05A(B/A) \leq 1.75$; and
forming a cover about the casing layer such that the fin-
ished golf ball has an Attini compression of from about 65
to about 120.

35. The method of claim 34, wherein the high acid divalent
ionomeric composition is blended with a filler selected from
the group consisting of fibers, flocks, flakes, glass flakes
microballoons, glass fibers, polymeric fiber, polymeric flock,
silica, clay, and combinations thereof.

36. The method of claim 34, wherein the high acid divalent
ionomeric composition is neutralized with a divalent cation
selected from the group consisting of zinc, magnesium, cal-
cium, and blends thereof.

37. The method of claim 34, wherein the high acid divalent
ionomeric composition is an ethylene/methacrylic acid
(E/MAA) copolymer having 19% methacrylic acid.

38. The method of claim 34, wherein the cover has a cover
inner surface adjacent the casing layer and a cover outer
surface surrounding the cover inner surface, wherein the
cover outer surface has a hardness $Q'$ of from about 50 shore
D to about 68 Shore D and wherein $Q' \leq Z$.

39. The method of claim 38, wherein hardness $X'$ is from
about 20 Shore D to about 45 Shore D, $Y'$ is from about 35
Shore D to about 56 Shore D and $Z'$ is from about 62 Shore D
to about 73 Shore D.

40. The method of claim 39, wherein hardness $Q'$ is from
about 50 Shore D to about 65 Shore D.

41. The method of claim 38, wherein hardness $X'$ is from
about 30 Shore D to about 40 Shore D, $Y'$ is from about 43
Shore D to about 54 Shore D and $Z'$ is from about 65 Shore D
to about 71 Shore D.

42. The method of claim 41, wherein hardness $Q'$ is from
about 55 Shore D to about 65 Shore D.

43. The method of claim 34, wherein hardness $X'$ is from
about 35 Shore D to about 38 Shore D, $Y'$ is from about 48
Shore D to about 50 Shore D and $Z'$ is from about 68 Shore D
to about 75 Shore D.

44. The method of claim 38, wherein hardness $Q'$ is from
about 60 Shore D to about 65 Shore D.