



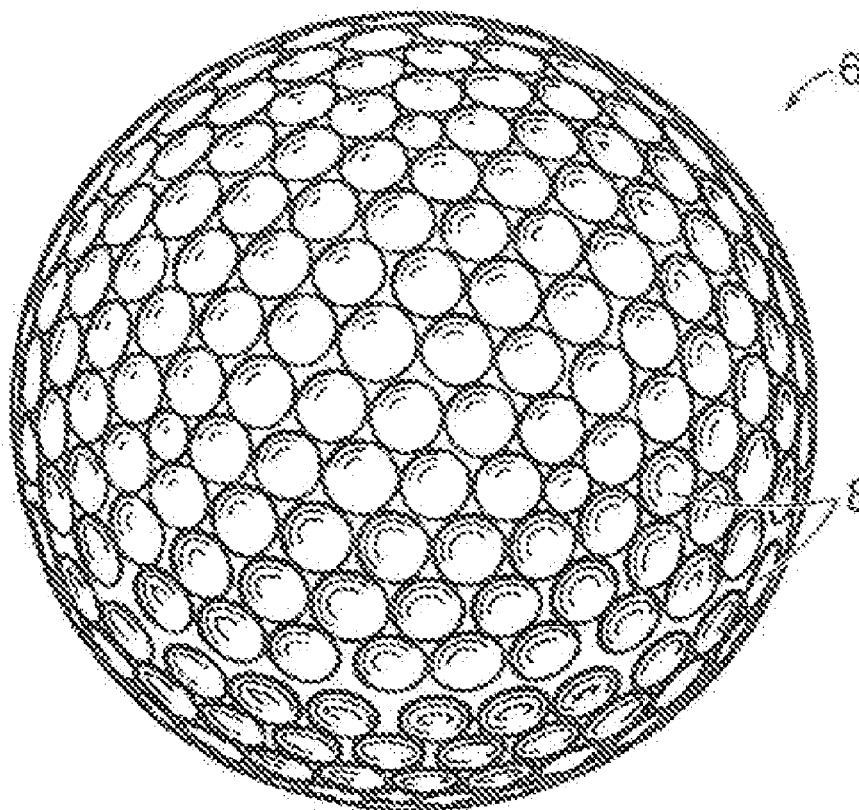
US 20170296881A1

(19) **United States**(12) **Patent Application Publication**
Hebert(10) **Pub. No.: US 2017/0296881 A1**(43) **Pub. Date: Oct. 19, 2017**(54) **METHODS FOR MAKING GOLF BALLS
HAVING HETEROGENEOUS LAYERS AND
RESULTING BALLS***A63B 37/00* (2006.01)*A63B 37/00* (2006.01)(52) **U.S. Cl.**CPC *A63B 45/00* (2013.01); *A63B 37/0094*
(2013.01); *A63B 37/0084* (2013.01); *A63B*
37/0032 (2013.01); *A63B 37/0074* (2013.01);
A63B 37/0075 (2013.01)(71) Applicant: **Acushnet Company**, Fairhaven, MA
(US)(72) Inventor: **Edmund A. Hebert**, Mattapoisett, MA
(US)(73) Assignee: **Acushnet Company**, Fairhaven, MA
(US)(21) Appl. No.: **15/099,727**(22) Filed: **Apr. 15, 2016****Publication Classification**(51) **Int. Cl.***A63B 45/00* (2006.01)*A63B 37/00* (2006.01)*A63B 37/00* (2006.01)*A63B 37/00* (2006.01)

(57)

ABSTRACT

Methods for making multi-piece golf balls having an outer cover, intermediate, or other layer comprising a heterogeneous composition are provided. The heterogeneous composition comprises a mixture of Compounds A and B. For example, the compounds can be different polyurethanes, ethylene acid copolymer ionomers, polyesters, polyamides, or any other suitable materials for making golf ball layers. Compounds having different hardness levels can be used. For example, the composition can comprise a mixture of hard and soft materials. The invention also encompasses golf balls made from such methods. The golf balls have good resiliency and impact durability along with other optimum playing performance properties.



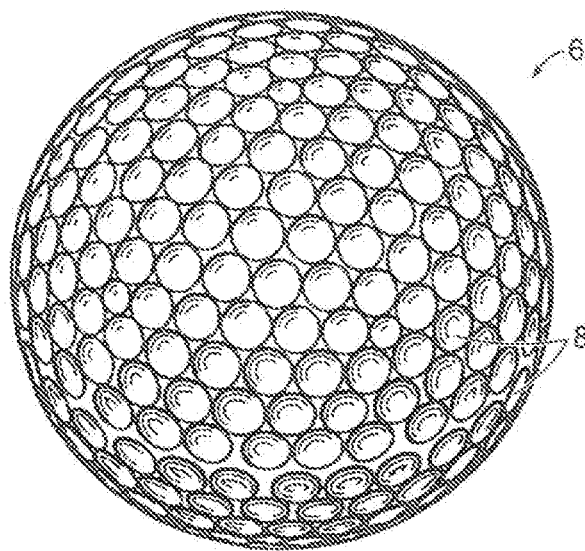


FIG. 1

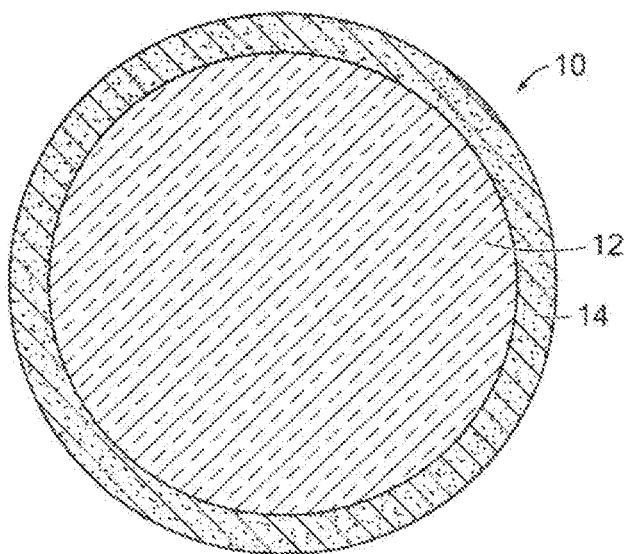


FIG. 2

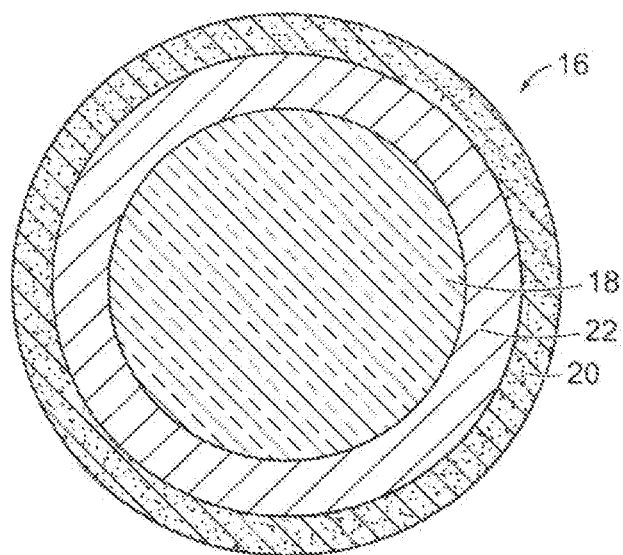


FIG. 3

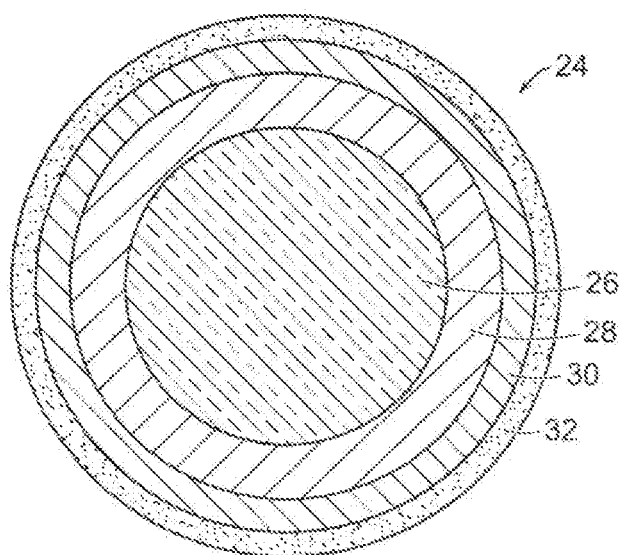


FIG. 4

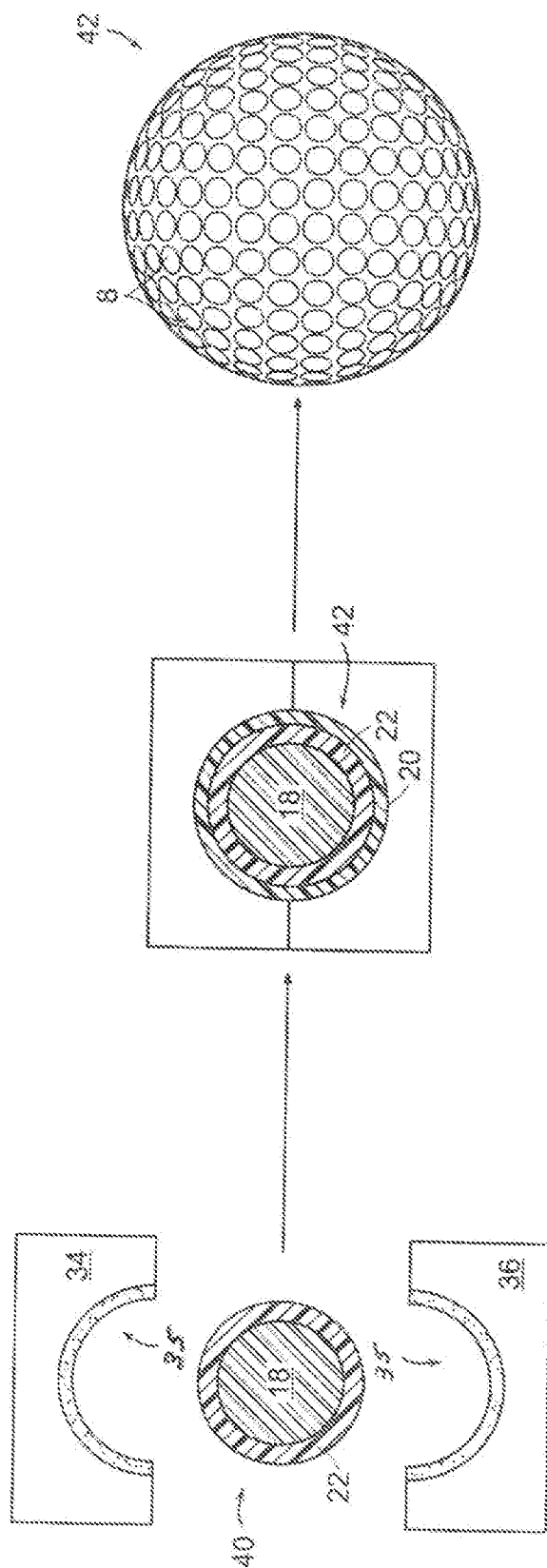


FIG. 5

METHODS FOR MAKING GOLF BALLS HAVING HETEROGENEOUS LAYERS AND RESULTING BALLS

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates generally to methods for making multi-piece golf balls having an outer cover or other layer comprising a heterogeneous composition. Particularly, in one example, the ball may have a layer made from a heterogeneous composition comprising a mixture of hard and soft ethylene acid copolymer ionomers. In another example, the ball may have a layer made from a heterogeneous composition comprising a mixture of aliphatic and aromatic polyurethanes. The invention also encompasses golf balls made from such methods.

Brief Review of the Related Art

[0002] Solid, multi-piece golf balls are commonly used by professional and recreational golfers today. For example, three-piece balls having an inner core, at least one intermediate layer surrounding the core, and an outer cover are popular. Different materials are used to make each of these layers. The materials are designed to impart more desirable playing performance properties to the golf ball.

[0003] For instance, a variety of materials may be used to make the inner core of the ball, particularly natural and synthetic rubbers such as styrene butadiene, polybutadiene, poly(cis-isoprene), and poly(trans-isoprene) or thermoplastic materials such as ethylene acid copolymer ionomers. The core is the primary source of resiliency for the golf ball and is often referred to as the engine of the ball. The ball may include one or more intermediate layers made from thermoplastic or thermoset resins such as polyamides, polyesters, ethylene acid copolymer ionomers, and the like.

[0004] The outer cover of the ball is designed to protect the core and provides the ball with durability, toughness, and cut/tear-resistance. The cover may comprise single or multiple layers. Conventional cover materials include polyurethanes, polyureas, and blends thereof, as well as highly neutralized ethylene acid copolymer ionomers (HNPs). The combination of core, intermediate layer(s), and cover provides the golf ball with its targeted performance properties.

[0005] It is well known that hard golf balls having relatively thick, hard outer covers can be made, and such balls generally have good durability, toughness, and impact-resistance. For example, hard ionomer resins can be used to make such covers. These thick-covered, ionomeric golf balls generally are harder and more resistant to wear and tear. The thick outer cover protects the core and such balls have good impact durability and cut/tear-resistance. However, these golf balls also can be overly stiff, and they tend to have low spin. Players tend to experience a harder feel when their club makes contact with such stiff balls. The player senses less control. The player has generally a less natural and comfortable sensation when striking such thick-covered, hard golf balls versus thin-covered, soft balls.

[0006] Thus, the golf industry has looked to develop golf balls having relatively thin cover layers. For example, golf balls having covers made from relatively soft polyurethanes, polyureas, and polyurethane/urea blends have been developed in recent years. For example, Hebert et al., U.S. Pat.

Nos. 6,132,324 and 5,885,172 disclose a method of forming a multi-layered golf ball comprising a core, inner cover layer, and outer cover layer. A castable reactive liquid polyurethane or polyurea material is introduced into mold cavities and then a ball subassembly (core and inner cover layer) is placed in one mold cavity. The upper and lower mold cavities are joined together. The polyurethane or polyurea material in the cavities encapsulates the ball subassembly and forms a thin cover for the ball.

[0007] In Lutz et al., U.S. Pat. Nos. 6,783,808 and 6,706,332 a method of coating a thin-layered over a golf ball component is provided. The method involves providing a polymer material; creating a polymer particulate from the polymer material; fluidizing the polymer particulate; and coating the golf ball component with a thin layer of the polymer material by placing the golf ball component within the fluidized particulate. Suitable polymers are described as including vinyl resins; polyolefins; polyurethanes; polyureas; polyamides; acrylic resins; and other thermoplastics and thermosets.

[0008] Conventional thin covers provide the ball with a softer feel, and the player can place a spin on the ball and better control its flight pattern. The softer cover feels more natural. Players sense more control with such softer, relatively thin-covered golf balls. There are drawbacks, however, with such thin-covered golf balls, because the balls tend to have less durability, toughness, and cut/tear-resistance. The ball may appear excessively worn with scuff marks, cuts, and tears after continuous play on the golf course. In addition, there can be drawbacks with using conventional methods such as casting and reaction injection molding ("RIM") to form thin cover layers. For example, casting processes may produce undesirable waste, and RIM mold parts may be difficult to position to achieve a uniform layer and leave pin marks on the cores or golf ball subassemblies. Thin layers may also be sprayed on the golf ball assemblies; however, spray applicators or nozzles can be clogged and the liquid compositions to be sprayed may also have undesirably high volatile organic components (VOC).

[0009] It would be desirable to have new methods for making golf balls having relatively thin cover layers. The present invention provides such methods along with the resulting golf balls. The balls have advantageous properties such as high impact durability, toughness, and cut/tear-resistance along with other benefits. Such covers, in combination with the cores, impart high resiliency to the golf balls. This allows players to generate greater initial ball velocity off the tee and achieve greater distance. At the same time, the relatively thin cover layers would provide the ball with a comfortable softness and natural feeling.

SUMMARY OF THE INVENTION

[0010] This invention relates to methods for making a multi-piece golf ball. Golf balls having various constructions can be made in accordance with this invention. In one preferred embodiment, the method comprises the steps of: i) introducing a first composition comprising Compound A into upper and lower mold members that define a mold cavity with a dimple pattern; ii) introducing a second composition comprising Compound B into the same upper and lower mold members so the first and second compositions are mixed together to form a heterogeneous composition comprising Compounds A and B; iii) placing a spherical core into the mold cavity; iv) applying heat and pressure to

the mold members so the heterogeneous composition encapsulates the core and forms an outer cover having a dimpled pattern; and v) removing the multi-piece golf ball from the mold.

[0011] In one preferred version, Compound A is an aliphatic polyurethane and Compound B is an aromatic polyurethane. In another preferred version, wherein Compound A and Compound B are O/X-type copolymers, wherein O is selected from the group consisting of ethylene and propylene, and X is an acid group selected from the group consisting of methacrylic acid, acrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid, and itaconic acid, and wherein at least 70% of the acid groups in Compound A are neutralized, and greater than 70% of the acid groups in Compound B are neutralized. For example, O can be ethylene and X can be methacrylic acid or acrylic acid. The core can be a single piece or multi-piece. For example, dual cores comprising an inner core and surrounding outer core layer, wherein at least one of the layers is formed from rubber, can be made.

[0012] The cover layers have different hardness levels. The outer cover layer formed from the heterogeneous composition has a midpoint hardness and outer hardness surface, and in one example, the hardness of the outer surface (for example, 35 to 90 Shore D) is greater than the hardness of the midpoint (for example, 30 to 80 Shore D) to define a positive hardness gradient. In another version, the hardness of the outer surface is the same or less than the hardness of the midpoint to define a zero or negative hardness gradient. The heterogeneous composition comprising Compounds A and B also can be used to form an intermediate layer in the ball. For example, the heterogeneous composition can be applied over the core so that it forms an intermediate layer. In this case, the core and surrounding intermediate layer comprise a ball subassembly, and a cover can be formed over the subassembly to form a multi-piece ball. The resulting golf balls have good resiliency and impact durability along with other optimum playing performance properties.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The novel features that are characteristic of the present invention are set forth in the appended claims. However, the preferred embodiments of the invention, together with further objects and attendant advantages, are best understood by reference to the following detailed description in connection with the accompanying drawings in which:

[0014] FIG. 1 is a front view of a multi-layered dimpled golf ball made in accordance with the present invention;

[0015] FIG. 2 is a cross-sectional view of a two-piece golf ball having an outer cover made of a heterogeneous composition in accordance with the present invention;

[0016] FIG. 3 is a cross-sectional view of a three-piece golf ball having an outer cover made of a heterogeneous composition in accordance with the present invention;

[0017] FIG. 4 is a cross-sectional view of a four-piece golf ball having an outer cover made of a heterogeneous composition in accordance with the present invention; and

[0018] FIG. 5 is a schematic diagram showing one embodiment for making a molded golf ball in accordance with the present invention.

DETAILED DESCRIPTION OF INVENTION

[0019] Golf balls having various constructions may be made in accordance with this invention. For example, golf balls having two-piece, three-piece, four-piece, and five-piece constructions with single or multi-layered cover materials may be made. Representative illustrations of such golf ball constructions are provided and discussed further below. The term, “layer” as used herein means generally any spherical portion of the golf ball. More particularly, in one version, a two-piece ball containing a core and surrounding cover also is made. In another version, a three-piece golf ball containing a core, intermediate layer, and cover layer is made. A four-piece golf ball containing a core, two intermediate layers, and cover layer also can be made. In yet another construction, a five-piece golf ball containing a core; three intermediate layers, and a cover layer may be made. As used herein, the term, “intermediate layer” means any layer of the ball disposed between the core and cover.

[0020] Heterogeneous Compositions

[0021] In the present invention, a heterogeneous composition is prepared and used to form an outer cover layer, intermediate layer, or any other layer for a golf ball. The intermediate layer may be considered an outer core layer or inner cover layer or any other layer disposed between the inner core and outer cover of the ball for purposes of this invention. The intermediate layer also may be referred to as a casing or mantle layer. The diameter and thickness of the different layers along with properties such as hardness and compression may vary depending upon the construction and desired playing performance properties of the golf ball.

[0022] In general, the method involves introducing a first composition comprising “Compound A” into upper and lower mold members. A second composition comprising “Compound B” is introduced into the upper and lower mold members containing the first composition. Thus, the first and second compositions are mixed together to form a heterogeneous composition comprising Compounds A and B. Although Compounds A and B are described primarily herein as being polyurethane materials, it should be understood that Compounds A and B can be any suitable material for making golf ball cover layers or intermediate layers in accordance with this invention.

[0023] For example, in producing an outer cover layer, a liquid mixture of reactive polyurethane prepolymer and chain-extender (curing agent) (“the first composition containing Compound A”, for example an aliphatic polyurethane as discussed further below”) can be poured into lower and upper mold members (half-shells), which may be pre-heated (normally at a temperature of about 125° to about 300° F.). The reactive polyurethane prepolymer and chain extender form a thin coating (skin) over the interior surfaces of the mold members.

[0024] Next, a liquid mixture of reactive polyurethane prepolymer and chain-extender (curing agent) (“the second polyurethane composition containing Compound B”, for example an aromatic polyurethane as discussed further below) is poured into the skin-coated lower and upper mold members. After this second polyurethane reactive mixture has resided in the lower mold member for a sufficient time period (typically about 40 to about 100 seconds), the golf ball core structure is lowered at a controlled speed into the reactive mixture. Ball suction cups can hold the core structure in place via reduced pressure or partial vacuum. After sufficient gelling of the reactive mixture (typically about 4 to

about 12 seconds), the vacuum is removed and the core is released into the mold cavity. Then, the upper mold member is mated with the lower mold member under sufficient pressure and heat. An exothermic reaction occurs when the polyurethane prepolymer and chain extender are mixed and this continues until the cover material encapsulates and solidifies around the core structure. Finally, the molded balls are cooled in the mold and removed when the molded cover is hard enough so that it can be handled without deforming.

[0025] In one embodiment, the heterogeneous composition may contain aromatic and aliphatic polyurethanes. In general, the aromatic polyurethane has good mechanical strength and cut/shear-resistance. However, one disadvantage with using aromatic isocyanates is the polymeric reaction product tends to have poor light stability and may discolor upon exposure to light, particularly ultraviolet (UV) light. On the other hand, the aliphatic polyurethane has good light stability but such polymers tend to have reduced mechanical strength and cut/shear-resistance. In the present invention, the heterogeneous composition may comprise both aromatic and aliphatic polyurethanes.

[0026] Moreover, the cover or other layer can be tailored such that there is a gradient of aromatic and aliphatic polyurethanes. For example, the aliphatic polyurethane composition can be dispensed into the mold cavity first and then the cavity may be gently hand-rocked so this composition skin-coats the interior surface of the cavity. Then, the aromatic polyurethane composition can be dispensed into the mold cavity so that it lies over the aliphatic polyurethane composition. The two separate and distinct polyurethane compositions are co-mingled. The polyurethane compositions are mixed to form a heterogeneous composition comprising aliphatic and aromatic polyurethanes.

[0027] Hard and Soft Compositions

[0028] In another embodiment, the heterogeneous composition may contain a mixture of relatively hard and soft materials. For example, a very soft, but shear-resistant material (Compound A) could be used. This material could be considered too soft or slow when used, by and in itself, as a cover material. However, it could be combined with a harder material (Compound B) that provides good resilience but lacks good shear-resistance. In mixing these materials, a relatively small shot of Compound A (softer material) could be added to the mold cavity and then a relatively large shot of Compound B (harder material) could be added over Compound A. There would be some co-mingling or mixing of materials to form a heterogeneous composition of Compounds A and B. In this example, there would be a thin layer of soft material at the outer surface of the cover, and a thicker layer of harder material below the outer surface region. Thus, the heterogeneous composition contains a hardness gradient, wherein the harder material is located in the outer surface region of the cover layer (or intermediate or other layer) and the softer material is located in the inner surface regions of the cover layer ((or intermediate or other layer) or vice versa).

[0029] As discussed above, in one embodiment, a heterogeneous composition comprising distinct polyurethane compounds is prepared. In another embodiment, the outer cover layer is made of a heterogeneous composition comprising a first ethylene acid copolymer ionomer and a second ethylene acid copolymer ionomer. In one particular example, one of the ionomer compound may be a relatively soft material and the other ionomer compound may be a relatively hard

material. For example, the first composition may contain an ethylene acid copolymer ionomer having less than 70% neutralization ("Compound A") and the second composition may contain an ethylene acid copolymer ionomer having greater than 70% neutralization ("Compound B").

[0030] In general, hardness gradients are described in Bulpett et al., U.S. Pat. Nos. 7,537,529 and 7,410,429, the disclosures of which are hereby incorporated by reference. Methods for measuring the hardness of the core, intermediate, and cover layers in the golf ball and determining the hardness gradients of the various layers are described in further detail below. The layers have positive, negative, or zero hardness gradients defined by hardness measurements made at the outer surface of the layer, for example, outer cover and radially inward towards the inner surface of the layer. These measurements are made typically at 2-mm increments as described in the test methods below. In general, the hardness gradient is determined by subtracting the hardness value at the innermost portion of the component being measured (for example, the inner surface of the cover layer) from the hardness value at the outer surface of the component being measured (for example, the outer surface of the cover layer).

[0031] Positive Hardness Gradient.

[0032] For example, if the hardness value of the cover layer's outer surface is greater than the hardness value of the cover layer's inner surface, the hardness gradient will be deemed "positive" (a larger number minus a smaller number equals a positive number.) For example, if the outer surface of the cover layer has a hardness of 67 Shore C and the inner surface of the inner cover layer has a hardness of 60 Shore C, then the cover layer has a positive hardness gradient of 7. Likewise, if the outer surface of the outer core layer has a greater hardness value than the inner surface of the outer core layer, the given outer core layer will be considered to have a positive hardness gradient.

[0033] Negative Hardness Gradient.

[0034] On the other hand, if the hardness value of the outer surface of the outer cover is less than the hardness value of the outer cover's inner surface (that is, the cover has an outer surface softer than its inner surface), the hardness gradient will be deemed "negative." For example, if the outer surface of the cover has a hardness of 68 Shore C and the inner surface of the cover has a hardness of 70 Shore C, then the cover has a negative hardness gradient of 2. Likewise, if the outer surface of the cover layer has a lesser hardness value than the inner surface of the outer core layer, the given outer core layer will be considered to have a negative hardness gradient.

[0035] Zero Hardness Gradient.

[0036] In another example, if the hardness value of the outer surface of the cover is substantially the same as the hardness value of the inner surface of the cover (that is, the outer surface and inner surface have about the same hardness), the hardness gradient will be deemed "zero." For example, if the outer surface of the cover and the inner surface of the cover each has a hardness of 65 Shore C, then the cover has a zero hardness gradient. Likewise, if the outer surface of the outer core layer has a hardness value approximately the same as the inner surface of the outer core layer, the outer core layer will be considered to have a zero hardness gradient.

[0037] More particularly, the term, "positive hardness gradient" as used herein means a hardness gradient of

positive 3 Shore D or greater, preferably 7 Shore D or greater, more preferably 10 Shore D, and even more preferably 20 Shore D or greater. The term, “zero hardness gradient” as used herein means a hardness gradient of less than 3 Shore D, preferably less than 1 Shore D and may have a value of zero or negative 1 to negative 10 Shore D. The term, “negative hardness gradient” as used herein means a hardness value of less than zero, for example, negative 3, negative 5, negative 7, negative 10, negative 15, or negative 20 or negative 25. The terms, “zero hardness gradient” and “negative hardness gradient” may be used herein interchangeably to refer to hardness gradients of negative 1 to negative 10.

[0038] In one example, the outer cover layer preferably has an outer surface hardness ($H_{\text{outer surface of cover}}$) of about 30 Shore D or greater, and more preferably within a range having a lower limit of about 30 or 34 or 37 or 40 or 42 or 44 or 46 or 48 or 50 or 52 and an upper limit of about 54 or 56 or 58 or 60 or 62 or 64 or 70 or 74 or 78 or 80 or 82 or 85 or 87 or 88 or 90 Shore D. The inner surface hardness of the cover layer ($H_{\text{inner surface of cover}}$) or midpoint hardness ($H_{\text{midpoint of cover}}$) of the cover layer, as measured in Shore D units, preferably has a lower limit of about 30 or 34 or 37 or 42 or 44 or 45 or 47 or 50 or 52 or 54 or 55 or 58 or 60 or 63 or 65 or 67 or 70 or 73 or 75 Shore C, and an upper limit of about 78 or 80 or 85 or 88 or 89 or 90 Shore D. The midpoint of the outer core layer is taken at a point equidistant from the inner surface and outer surface of the layer to be measured. Once one or more core layers surround a layer of interest, the exact midpoint may be difficult to determine, therefore, for the purposes of the present invention, the measurement of “midpoint” hardness of a layer is taken within plus or minus 1 mm of the measured midpoint of the layer.

[0039] In one embodiment, the outer surface hardness of the outer cover layer ($H_{\text{outer surface of cover}}$), is less than the inner surface hardness ($H_{\text{inner surface of cover}}$) or midpoint hardness ($H_{\text{midpoint of cover}}$), of the outer cover by at least 3 Shore D units and more preferably by at least 5 Shore D to provide a zero or negative hardness gradient.

[0040] In a second embodiment, the outer surface hardness of the outer core layer ($H_{\text{outer surface of cover}}$), is greater than the inner surface hardness ($H_{\text{inner surface of hardness}}$) or midpoint hardness ($H_{\text{midpoint of cover}}$), of the cover by at least 3 Shore D units and more preferably by at least 5 Shore D to provide a positive hardness gradient.

[0041] Other Components in Golf Ball Construction

[0042] The solid cores for the golf balls of this invention may be made using any suitable conventional technique such as, for example, compression or injection molding. Typically, the cores are formed by compression molding a slug of uncured or lightly cured rubber material into a spherical structure. Prior to forming the cover layer, the core structure may be surface-treated to increase the adhesion between its outer surface and adjacent layer. Such surface-treatment may include mechanically or chemically-abrading the outer surface of the core. For example, the core may be subjected to corona-discharge, plasma-treatment, silane-dipping, or other treatment methods known to those in the art.

[0043] The core sub-assembly may comprise an inner core and surrounding outer core layer. That is, single-layered cores having a single inner core and multi-layered cores having an inner core and outer core layer may be made in accordance with this invention. The ball sub-assembly may

comprise the core structure (for example, single-layered core or multi-layered core) and any overlying intermediate layers. After the golf balls have been removed from the mold, they may be subjected to finishing steps such as flash-trimming, surface-treatment, marking, coating, and the like using techniques known in the art. For example, in traditional white-colored golf balls, the white-pigmented cover may be surface-treated using a suitable method such as, for example, corona, plasma, or ultraviolet (UV) light-treatment. Then, indicia such as trademarks, symbols, logos, letters, and the like may be printed on the ball's cover using pad-printing, ink-jet printing, dye-sublimation, or other suitable printing methods. Clear surface coatings (for example, primer and top-coats), which may contain a fluorescent whitening agent, are applied to the cover. The resulting golf ball has a glossy and durable surface finish.

[0044] In another finishing process, the golf balls are painted with one or more paint coatings. For example, white primer paint may be applied first to the surface of the ball and then a white top-coat of paint may be applied over the primer. Of course, the golf ball may be painted with other colors, for example, red, blue, orange, and yellow. Markings such as trademarks and logos may be applied to the painted cover of the golf ball. Finally, a clear surface coating may be applied to the cover to provide a shiny appearance and protect any logos and other markings printed on the ball.

[0045] Referring to FIG. 1, one version of a golf ball that can be made in accordance with this invention is generally indicated at (6). Various patterns and geometric shapes of dimples (8) are used to modify the aerodynamic properties of the golf ball (6). The dimples (8) can be arranged on the outer surface of the ball (6) in various patterns to modify the aerodynamic properties of the ball as discussed in detail below.

[0046] As discussed above, the lower and upper mold cavities are mated together to form the outer cover layer for the ball. The outer cover material encapsulates the inner ball. The mold cavities used to form the outer layer have interior dimple cavity details. The cover material conforms to the interior geometry of the mold cavities to form a dimple pattern on the surface of the ball. The mold cavities may have any suitable dimple arrangement such as, for example, icosahedral, octahedral, cube-octahedral, dipyrmaid, and the like. In addition, the dimples may be circular, oval, triangular, square, pentagonal, hexagonal, heptagonal, octagonal, and the like. Possible cross-sectional shapes include, but are not limited to, circular arc, truncated cone, flattened trapezoid, and profiles defined by a parabolic curve, ellipse, semi-spherical curve, saucer-shaped curve, sine or catenary curve, or conical curve. Other possible dimple designs include dimples within dimples, constant depth dimples, or multi-lobe dimples, as disclosed in U.S. Pat. No. 6,749,525. It also should be understood that more than one shape or type of dimple may be used on a single ball, if desired.

[0047] The use of various dimple patterns and profiles provides a relatively effective way to modify the aerodynamic characteristics of a golf ball. Suitable dimple patterns include, for example, icosahedron-based pattern, as described in U.S. Pat. No. 4,560,168; octahedral-based dimple patterns as described in U.S. Pat. No. 4,960,281; and tetrahedron-based patterns as described in co-assigned, co-pending, U.S. patent application Ser. No. 12/894,827, the disclosure of which is hereby incorporated by reference. Other tetrahedron-based dimple designs are shown in co-

assigned, co-pending design applications D Ser. No. 29/362,123; D Ser. No. 29/362,124; D Ser. No. 29/362,125; and D Ser. No. 29/362,126, the disclosures of which are hereby incorporated by reference.

[0048] The total number of dimples on the ball, or dimple count, may vary depending such factors as the sizes of the dimples and the pattern selected. In general, the total number of dimples on the ball preferably is between about 100 to about 1000 dimples, although one skilled in the art would recognize that differing dimple counts within this range can significantly alter the flight performance of the ball. In one embodiment, the dimple count is about 300-360 dimples. In one embodiment, the dimple count on the ball is about 360-400 dimples.

[0049] Referring to FIG. 2, a cross-sectional view of a two-piece golf ball (10) having a solid inner core (12) and outer cover (14) made of the heterogeneous composition of this invention is shown. The outer cover (14) contains numerous dimples as shown in FIG. 1. To make the finished golf ball, the cover can be painted white or another color. First, a primer coat can be applied to the cover and then a pigmented paint can be applied over the primer. Typically, a custom logo, symbol, or other mark is ink-printed onto the painted surface and a clear, protective top coat is applied over the printed mark to provide a glossy finish. In other instances, the cover material may contain white pigment or a different colored concentrate. In FIG. 3, a cross-sectional view of a three-piece golf ball (16) having a solid core (18) and cover (20) made of the heterogeneous composition of this invention is shown. An intermediate layer (22) is disposed between the core (18) and cover layer (20). Turning to FIG. 4, a golf ball (24) having a multi-layered cover is shown. The golf ball (24) includes a solid core (26) and intermediate layer (28). The inner cover layer (30) is made of a conventional thermoplastic or thermoset polymer composition, while the outer cover (32) is made of the heterogeneous composition of this invention.

[0050] Turning to FIG. 5, one embodiment of the molding method of this invention is shown, wherein the heterogeneous composition is dispensed into the interior surfaces of an upper mold member (34) and lower mold member (36) which define a mold cavity for holding a golf ball subassembly (40). The heterogeneous composition (35), which will be used to form the outer cover layer, is introduced into the mold members. In FIG. 5, the golf ball subassembly (40) includes a solid core (18) surrounded by a casing (22). The core (18) can be made of a polybutadiene rubber and the casing (22) can be made of an ionomer resin. The ball subassembly (40) is placed into the mold cavity defined by the upper and lower mold halves (34, 36). This step can be performed manually or automatically by machine. Next, the mold members (34, 36) are joined and a sufficient amount of heat and pressure is applied to the mold so the heterogeneous composition (35) fuses and encapsulates the ball subassembly (40). Thus, an outer cover (20) comprising a heterogeneous outer cover layer is formed. The resulting molded golf ball (42) is preferably cooled before it is removed from the mold.

[0051] It should be understood that the golf balls shown in FIGS. 1-5 are for illustrative purposes only and not meant to be restrictive. Other golf ball constructions can be made in accordance with this invention.

[0052] In one embodiment, as discussed above, a cover layer comprising a heterogeneous composition of aliphatic

and aromatic polyurethanes is made. The cover layer, in this embodiment, is a single layer comprising Compounds A and B (aliphatic and aromatic polyurethane) so it has the properties of two layers. The single layer is essentially "split" as a heterogeneous composition, wherein each compound contributes to the overall good physical and playing properties of the ball. For example, the cover layer has good durability and toughness. Furthermore, the cover layer has good light stability. The cover layer has high ultraviolet light (UV)-resistance and is less likely to discolor upon exposure to sunlight. Thus, the golf balls of this invention have good light stability without sacrificing important mechanical properties such as durability and high cut/shear-resistance.

[0053] The method of this invention is particularly effective in providing golf balls having a very thin outer cover layer. For example, the thickness of this outer cover layer can be in the range of about 0.004 to about 0.050 inches. In one preferred embodiment, the thickness is about 0.006 to about 0.040 inches or about 0.008 to about 0.030 inches and more preferably about 0.012 to about 0.018 inches.

[0054] When these methods are used to make the intermediate layer, the thickness of that layer can be in the range of about 0.015 inches to about 0.100 inches. In one preferred embodiment, the thickness is in the range of about 0.020 inches to about 0.080 inches, and more preferably about 0.030 inches to about 0.050 inches.

[0055] The United States Golf Association ("USGA") has set total weight limits for golf balls. Particularly, the USGA has established a maximum weight of 45.93 g (1.62 ounces) for golf balls. There is no lower weight limit. In addition, the USGA requires that golf balls used in competition have a diameter of at least 1.68 inches. There is no upper limit so many golf balls have an overall diameter falling within the range of about 1.68 to about 1.80 inches. The golf ball diameter is preferably about 1.68 to 1.74 inches, more preferably about 1.68 to 1.70 inches. In accordance with the present invention, the weight, diameter, and thickness of the core and cover layers may be adjusted, as needed, so the ball meets USGA specifications of a maximum weight of 1.62 ounces and a minimum diameter of at least 1.68 inches. For play outside of the USGA rules, the ball can have a greater weight than 1.62 ounces and can be of any diameter size.

[0056] A wide variety of materials may be used for forming the outer cover and intermediate layers in accordance with this invention including, for example, polyurethanes; polyureas; copolymers, blends and hybrids of polyurethane and polyurea; olefin-based copolymer ionomer resins (for example, Surlyn® ethylene acid copolymer ionomer resins and DuPont HPF® 1000 and HPF® 2000, commercially available from DuPont; Iotek® ionomers, commercially available from ExxonMobil Chemical Company; Amplify® IO ionomers of ethylene acrylic acid copolymers, commercially available from The Dow Chemical Company; and Clarix® ionomer resins, commercially available from A. Schulman Inc.); polyethylene, including, for example, low density polyethylene, linear low density polyethylene, and high density polyethylene; polypropylene; rubber-toughened olefin polymers; acid copolymers, for example, poly(meth)acrylic acid, which do not become part of an ionomeric copolymer; plastomers; styrene/butadiene/styrene block copolymers; styrene/ethylene-butylene/styrene block copolymers; dynamically vulcanized elastomers; copolymers of ethylene and vinyl acetates; copolymers of ethylene and methyl acrylates; polyvinyl

chloride resins; polyamides, poly(amide-ester) elastomers, and graft copolymers of ionomer and polyamide including, for example, Pebax® thermoplastic polyether block amides, commercially available from Arkema Inc; cross-linked trans-polyisoprene and blends thereof; polyester-based thermoplastic elastomers, such as Hytrel®, commercially available from DuPont or RiteFlex®, commercially available from Ticona Engineering Polymers; polyurethane-based thermoplastic elastomers, such as Elastollan®, commercially available from BASF; polycarbonate/polyester blends such as Xylex®, available from SABIC Innovative Plastics; maleic anhydride-grafted polymers such as Fusabond®, available from DuPont; and mixtures of the foregoing materials. Castable polyurethanes, polyureas, and hybrids of polyurethanes-polyureas are particularly desirable because these materials can be used to make a golf ball having high resiliency and a soft feel. By the term, “hybrids of polyurethane and polyurea,” it is meant to include copolymers and blends thereof.

[0057] The compositions used to make the cover layer may contain a wide variety of fillers and additives to impart specific properties to the ball. For example, relatively heavy-weight and light-weight metal fillers such as, particulate; powders; flakes; and fibers of copper, steel, brass, tungsten, titanium, aluminum, magnesium, molybdenum, cobalt, nickel, iron, lead, tin, zinc, barium, bismuth, bronze, silver, gold, and platinum, and alloys and combinations thereof may be used to adjust the specific gravity of the ball. Other additives and fillers include, but are not limited to, optical brighteners, coloring agents, fluorescent agents, whitening agents, UV absorbers, light stabilizers, surfactants, processing aids, antioxidants, stabilizers, softening agents, fragrance components, plasticizers, impact modifiers, titanium dioxide, clay, mica, talc, glass flakes, milled glass, and mixtures thereof.

[0058] Polyurethanes

[0059] As discussed above, in one preferred embodiment, the outer cover layer is made of a heterogeneous polyurethane composition comprising a first polyurethane composition and a second compound composition. The intermediate layer also may be made of a heterogeneous polyurethane composition. For example, the first polyurethane composition may contain aliphatic polyurethane (“Compound A”) and the second polyurethane composition may contain aromatic polyurethane (“Compound B”).

[0060] In general, polyurethane compositions contain urethane linkages formed by reacting an isocyanate group (—N=C=O) with a hydroxyl group (OH). The polyurethanes are produced by the reaction of a multi-functional isocyanate (NCO—R—NCO) with a long-chain polyol having terminal hydroxyl groups (OH—OH) in the presence of a catalyst and other additives. The chain length of the polyurethane prepolymer is extended by reacting it with short-chain diols (OH—R'—OH). The resulting polyurethane has elastomeric properties because of its “hard” and “soft” segments, which are covalently bonded together.

[0061] In one embodiment, the cover layer comprises aliphatic polyurethane, which is preferably formed by reacting an aliphatic diisocyanate with a polyol. Suitable aliphatic diisocyanates that may be used in accordance with this invention include, for example, isophorone diisocyanate (IPDI), 1,6-hexamethylene diisocyanate (HDI), 4,4'-dicyclohexylmethane diisocyanate (“H₁₂ MDI”), meta-tetram-

ethylxylylene diisocyanate (TMXDI), trans-cyclohexane diisocyanate (CHDI), and homopolymers and copolymers and blends thereof.

[0062] The cover layer also comprises aromatic polyurethane, which is preferably formed by reacting an aromatic diisocyanate with a polyol. Suitable aromatic diisocyanates that may be used in accordance with this invention include, for example, toluene 2,4-diisocyanate (TDI), toluene 2,6-diisocyanate (TDI), 4,4'-methylene diphenyl diisocyanate (MDI), 2,4'-methylene diphenyl diisocyanate (MDI), polymeric methylene diphenyl diisocyanate (PMDI), p-phenylene diisocyanate (PPDI), m-phenylene diisocyanate (PDI), naphthalene 1,5-diisocyanate (NDI), naphthalene 2,4-diisocyanate (NDI), p-xylene diisocyanate (XDI), and homopolymers and copolymers and blends thereof. The aromatic isocyanates are able to react with the hydroxyl or amine compounds and form a durable and tough polymer having a high melting point.

[0063] Any suitable polyol may be reacted with the diisocyanate compound. Exemplary polyols include, but are not limited to, polyether polyols, hydroxy-terminated polybutadiene (including partially/fully hydrogenated derivatives), polyester polyols, polycaprolactone polyols, and polycarbonate polyols. In one preferred embodiment, the polyol includes polyether polyol. Examples include, but are not limited to, polytetramethylene ether glycol (PTMEG), polyethylene propylene glycol, polyoxypropylene glycol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds and substituted or unsubstituted aromatic and cyclic groups. One preferred polyol is PTMEG. In another preferred embodiment, polyester polyols are used including, but not limited to, polyethylene adipate glycol; polybutylene adipate glycol; polyethylene propylene adipate glycol; o-phthalate-1,6-hexanediol; poly (hexamethylene adipate) glycol; and mixtures thereof. In still another embodiment, polycaprolactone polyols are used.

[0064] There are two basic techniques that can be used to make the polyurethane compositions of this invention: a) one-shot technique, and b) prepolymer technique. In the one-shot technique, the diisocyanate, polyol, and hydroxyl-terminated chain-extender (curing agent) are reacted in one step. On the other hand, the prepolymer technique involves a first reaction between the diisocyanate and polyol compounds to produce a polyurethane prepolymer, and a subsequent reaction between the prepolymer and hydroxyl-terminated chain-extender. As a result of the reaction between the isocyanate and polyol compounds, there will be some unreacted NCO groups in the polyurethane prepolymer. The prepolymer should have less than 14% unreacted NCO groups. Preferably, the prepolymer has no greater than 8.5% unreacted NCO groups, more preferably from 2.5% to 8%, and most preferably from 5.0% to 8.0% unreacted NCO groups. As the weight percent of unreacted isocyanate groups increases, the hardness of the composition also generally increases.

[0065] Either the one-shot or prepolymer method may be employed to produce the polyurethane compositions of the invention. In one embodiment, the one-shot method is used, wherein the isocyanate compound is added to a reaction vessel and then a curative mixture comprising the polyol and curing agent is added to the reaction vessel. The components are mixed together so that the molar ratio of isocyanate groups to hydroxyl groups is in the range of about 1.01:1.00

to about 1.10:1.00. Preferably, the molar ratio is greater than 1.05:1.00. For example, the molar ratio can be in the range of 1.07:1.00 to 1.10:1.00. In a second embodiment, the prepolymer method is used. In general, the prepolymer technique is preferred because it provides better control of the chemical reaction. The prepolymer method provides a more homogeneous mixture resulting in a more consistent polymer composition. The one-shot method results in a mixture that is inhomogeneous (more random) and affords the manufacturer less control over the molecular structure of the resultant composition.

[0066] The polyurethane compositions can be formed by chain-extending the polyurethane prepolymer with a single chain-extender or blend of chain-extenders as described further below. Thermoset compositions, on the other hand, are cross-linked polymers and are typically produced from the reaction of the isocyanate blend and polyols at normally a 1.05:1 stoichiometric ratio. In general, thermoset polyurethane compositions are easier to prepare than thermoplastic polyurethanes.

[0067] As discussed above, the polyurethane prepolymer can be chain-extended by reacting it with a single chain-extender or blend of chain-extenders. In general, the prepolymer can be reacted with hydroxyl-terminated curing agents, amine-terminated curing agents, and mixtures thereof. The curing agents extend the chain length of the prepolymer and build-up its molecular weight. Normally, the prepolymer and curing agent are mixed so the isocyanate groups and hydroxyl or amine groups are mixed at a 1.05:1.00 stoichiometric ratio.

[0068] A catalyst may be employed to promote the reaction between the isocyanate and polyol compounds for producing the prepolymer or between prepolymer and chain-extender during the chain-extending step. Preferably, the catalyst is added to the reactants before producing the prepolymer. Suitable catalysts include, but are not limited to, bismuth catalyst; zinc octoate; stannous octoate; tin catalysts such as bis-butyltin dilaurate, bis-butyltin diacetate, stannous octoate; tin (II) chloride, tin (IV) chloride, bis-butyltin dimethoxide, dimethyl-bis[1-oxondecyl]oxy]stannane, di-n-octyltin bis-isooctyl mercaptoacetate; amine catalysts such as triethylenediamine, triethylamine, and tributylamine; organic acids such as oleic acid and acetic acid; delayed catalysts; and mixtures thereof. The catalyst is preferably added in an amount sufficient to catalyze the reaction of the components in the reactive mixture. In one embodiment, the catalyst is present in an amount from about 0.001 percent to about 1 percent, and preferably 0.1 to 0.5 percent, by weight of the composition.

[0069] The hydroxyl chain-extending (curing) agents are preferably selected from the group consisting of ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; 2-methyl-1,3-propanediol; 2-methyl-1,4-butanediol; monoethanolamine; diethanolamine; triethanolamine; monoisopropanolamine; diisopropanolamine; dipropylene glycol; polypropylene glycol; 1,2-butanediol; 1,3-butanediol; 1,4-butanediol; 2,3-butanediol; 2,3-dimethyl-2,3-butanediol; trimethylolpropane; cyclohexyldimethylol; triisopropanolamine; N,N,N',N'-tetra-(2-hydroxypropyl)-ethylene diamine; diethylene glycol bis-(aminopropyl) ether; 1,5-pentanediol; 1,6-hexanediol; 1,3-bis-(2-hydroxyethoxy) cyclohexane; 1,4-cyclohexyldimethylol; 1,3-bis-[2-(2-hydroxyethoxy) ethoxy]cyclohexane; 1,3-bis-{2-[2-(2-hydroxyethoxy) ethoxy]ethoxy}cyclohexane;

trimethylolpropane; polytetramethylene ether glycol (PT-MEG), preferably having a molecular weight from about 250 to about 3900; and mixtures thereof.

[0070] Suitable amine chain-extending (curing) agents that can be used in chain-extending the polyurethane prepolymer include, but are not limited to, unsaturated diamines such as 4,4'-diamino-diphenylmethane (i.e., 4,4'-methylenedianiline or "MDA"), m-phenylenediamine, p-phenylenediamine, 1,2- or 1,4-bis(sec-butylamino)benzene, 3,5-diethyl-(2,4- or 2,6-) toluenediamine or "DETDA", 3,5-dimethylthio-(2,4- or 2,6-)toluenediamine, 3,5-diethylthio-(2,4- or 2,6-)toluenediamine, 3,3'-dimethyl-4,4'-diaminodiphenylmethane, 3,3'-diethyl-5,5'-dimethyl 4,4'-diaminodiphenylmethane (i.e., 4,4'-methylene-bis(2-ethyl-6-methylbenzeneamine)), 3,3'-dichloro-4,4'-diaminodiphenylmethane (i.e., 4,4'-methylene-bis(2-chloroaniline) or "MOCDA"), 3,3',5,5'-tetraethyl-4,4'-diaminodiphenylmethane (i.e., 4,4'-methylene-bis(2,6-diethylaniline), 2,2'-dichloro-3,3',5,5'-tetraethyl-4,4'-diaminodiphenylmethane (i.e., 4,4'-methylene-bis(3-chloro-2,6-diethylaniline) or "MCDEA"), 3,3'-diethyl-5,5'-dichloro-4,4'-diaminodiphenylmethane, or "MDEA"), 3,3'-dichloro-2,2',6,6'-tetraethyl-4,4'-diaminodiphenylmethane, 3,3'-dichloro-4,4'-diaminodiphenylmethane, 4,4'-methylene-bis(2,3-dichloroaniline) (i.e., 2,2',3,3'-tetrachloro-4,4'-diaminodiphenylmethane or "MDCA"), 4,4'-bis(sec-butylamino)-diphenylmethane, N,N'-dialkylamino-diphenylmethane, trimethyleneglycol-di(p-aminobenzoate), polyethyleneglycol-di(p-aminobenzoate), polytetramethyleneglycol-di(p-aminobenzoate); saturated diamines such as ethylene diamine, 1,3-propylene diamine, 2-methyl-pentamethylene diamine, hexamethylene diamine, 2,2,4- and 2,4,4-trimethyl-1,6-hexane diamine, imino-bis(propylamine), imido-bis(propylamine), methyl-imino-bis(propylamine) (i.e., N-(3-aminopropyl)-N-methyl-1,3-propanediamine), 1,4-bis(3-aminopropoxy)butane (i.e., 3,3'-[1,4-butanediylbis(oxy)bis]-1-propanamine), diethyleneglycol-bis(propylamine) (i.e., diethyleneglycol-di(aminopropyl)ether), 4,7,10-trioxatridecane-1,13-diamine, 1-methyl-2,6-diamino-cyclohexane, 1,4-diamino-cyclohexane, poly(oxyethylene-oxypropylene) diamines, 1,3- or 1,4-bis(methylamino)-cyclohexane, isophorone diamine, 1,2- or 1,4-bis(sec-butylamino)-cyclohexane, N,N'-diisopropyl-isophorone diamine, 4,4'-diamino-dicyclohexylmethane, 3,3'-dimethyl-4,4'-diamino-dicyclohexylmethane, 3,3'-dichloro-4,4'-diamino-dicyclohexylmethane, N,N'-dialkylamino-dicyclohexylmethane, polyoxyethylene diamines, 3,3'-diethyl-5,5'-dimethyl-4,4'-diamino-dicyclohexylmethane, polyoxypropylene diamines, 3,3'-diethyl-5,5'-dichloro-4,4'-diamino-dicyclohexylmethane, polytetramethylene ether diamines, 3,3',5,5'-tetraethyl-4,4'-diamino-dicyclohexylmethane (i.e., 4,4'-methylene-bis(2,6-diethylaminocyclohexane)), 3,3'-dichloro-4,4'-diamino-dicyclohexylmethane, 2,2'-dichloro-3,3',5,5'-tetraethyl-4,4'-diamino-dicyclohexylmethane, (ethylene oxide)-capped polyoxypropylene ether diamines, 2,2',3,3'-tetrachloro-4,4'-diamino-dicyclohexylmethane, 4,4'-bis(sec-butylamino)-dicyclohexylmethane; triamines such as diethylene triamine, dipropylene triamine, (propylene oxide)-based triamines (i.e., polyoxypropylene triamines), N-(2-aminoethyl)-1,3-propylenediamine (i.e., N₃-amine), glycerin-based triamines, (all saturated); tetramines such as N,N'-bis(3-aminopropyl)ethylene diamine (i.e., N₄-amine) (both saturated), triethylene tetramine; and other polyamines such as tetraethylene pentamine (also saturated). One suitable

amine-terminated chain-extending agent is Ethacure 300™ (dimethylthiotoluenediamine or a mixture of 2,6-diamino-3,5-dimethylthiotoluene and 2,4-diamino-3,5-dimethylthiotoluene.) The amine curing agents used as chain extenders normally have a cyclic structure and a low molecular weight (250 or less).

[0071] When the polyurethane prepolymer is reacted with hydroxyl-terminated curing agents during the chain-extending step, as described above, the resulting polyurethane composition contains urethane linkages. On the other hand, when the polyurethane prepolymer is reacted with amine-terminated curing agents during the chain-extending step, any excess isocyanate groups in the prepolymer will react with the amine groups in the curing agent. The resulting polyurethane composition contains urethane and urea linkages and may be referred to as a polyurethane/urea hybrid. The concentration of urethane and urea linkages in the hybrid composition may vary. In general, the hybrid composition may contain a mixture of about 10 to 90% urethane and about 90 to 10% urea linkages.

[0072] As discussed above, a heterogeneous polyurethane composition comprising aromatic and aliphatic polyurethanes may be used in accordance with this invention. For example, the aromatic polyurethane may be used in an amount of at least about 10% by weight based on total weight of composition and is generally present in an amount of about 10% to about 100%, or an amount within a range having a lower limit of 20% or 30% or 40% or 50% or 60% or 70% or 75% and an upper limit of 80% or 85% or 90% or 95% or 100%. Preferably, the concentration of aromatic polyurethane is at least 40% and more preferably about 40% to about 100%, and even more preferably at least 75% or about 75% to about 100%. Meanwhile, the aliphatic polyurethane may be used in an amount of at least about 10% by weight based on total weight of composition and is generally present in an amount of about 10% to about 100%, or an amount within a range having a lower limit of 20% or 30% or 40% or 50% or 60% or 70% or 75% and an upper limit of 80% or 85% or 90% or 95% or 100%. Preferably, the concentration of aliphatic polyurethane is at least 40% and more preferably about 40% to about 100%, and even more preferably at least 75% or about 75% to about 100%.

[0073] In addition, the polyurethane compositions may contain fillers, additives, and other ingredients that do not detract from the properties of the final composition. These additional materials include, but are not limited to, catalysts, wetting agents, coloring agents, optical brighteners, cross-linking agents, whitening agents such as titanium dioxide and zinc oxide, ultraviolet (UV) light absorbers, hindered amine light stabilizers, defoaming agents, processing aids, surfactants, and other conventional additives. Other suitable additives include antioxidants, stabilizers, softening agents, plasticizers, including internal and external plasticizers, impact modifiers, foaming agents, density-adjusting fillers, reinforcing materials, compatibilizers, and the like. Some examples of useful fillers include zinc oxide, zinc sulfate, barium carbonate, barium sulfate, calcium oxide, calcium carbonate, clay, tungsten, tungsten carbide, silica, and mixtures thereof. Rubber regrind (recycled core material) and polymeric, ceramic, metal, and glass microspheres also may be used. Generally, the additives will be present in the composition in an amount between about 1 and about 70 weight percent based on total weight of the composition depending upon the desired properties.

[0074] Ethylene Acid Copolymers

[0075] As discussed above, in one preferred embodiment, a heterogeneous polyurethane composition may be made. In another preferred embodiment, the outer cover layer is made of a heterogeneous composition comprising a first ethylene acid copolymer ionomer and a second ethylene acid copolymer ionomer. The intermediate layer also may be made of a heterogeneous ethylene acid copolymer ionomer composition. For example, the first composition may contain an ethylene acid copolymer ionomer having less than 70% neutralization ("Compound A") and the second composition may contain an ethylene acid copolymer ionomer having greater than 70% neutralization ("Compound B").

[0076] Suitable ionomer compositions include partially-neutralized ionomers and highly-neutralized ionomers (HNPs), including ionomers formed from blends of two or more partially-neutralized ionomers, blends of two or more highly-neutralized ionomers, and blends of one or more partially-neutralized ionomers with one or more highly-neutralized ionomers. For purposes of the present disclosure, "HNP" refers to an acid copolymer after at least 70% of all acid groups present in the composition are neutralized.

[0077] Preferred ionomers are salts of O/X- and O/X/Y-type acid copolymers, wherein O is an α -olefin, X is a C_3 - C_8 α,β -ethylenically unsaturated carboxylic acid, and Y is a softening monomer. O is preferably selected from ethylene and propylene. X is preferably selected from methacrylic acid, acrylic acid, ethacrylic acid, crotonic acid, and itaconic acid. Methacrylic acid and acrylic acid are particularly preferred. Y is preferably selected from (meth) acrylate and alkyl (meth) acrylates wherein the alkyl groups have from 1 to 8 carbon atoms, including, but not limited to, n-butyl (meth) acrylate, isobutyl (meth) acrylate, methyl (meth) acrylate, and ethyl (meth) acrylate.

[0078] Preferred O/X and O/X/Y-type copolymers include, without limitation, ethylene acid copolymers, such as ethylene/(meth)acrylic acid, ethylene/(meth)acrylic acid/maleic anhydride, ethylene/(meth)acrylic acid/maleic acid mono-ester, ethylene/maleic acid, ethylene/maleic acid mono-ester, ethylene/(meth)acrylic acid/n-butyl (meth)acrylate, ethylene/(meth)acrylic acid/iso-butyl (meth)acrylate, ethylene/(meth)acrylic acid/methyl (meth)acrylate, ethylene/(meth)acrylic acid/ethyl (meth)acrylate terpolymers, and the like. The term, "copolymer," as used herein, includes polymers having two types of monomers, those having three types of monomers, and those having more than three types of monomers. Preferred α,β -ethylenically unsaturated mono- or dicarboxylic acids are (meth) acrylic acid, ethacrylic acid, maleic acid, crotonic acid, fumaric acid, itaconic acid. (Meth) acrylic acid is most preferred. As used herein, "(meth) acrylic acid" means methacrylic acid and/or acrylic acid. Likewise, "(meth) acrylate" means methacrylate and/or acrylate.

[0079] In a particularly preferred version, highly neutralized E/X- and E/X/Y-type acid copolymers, wherein E is ethylene, X is a C_3 - C_8 α,β -ethylenically unsaturated carboxylic acid, and Y is a softening monomer are used. X is preferably selected from methacrylic acid, acrylic acid, ethacrylic acid, crotonic acid, and itaconic acid. Methacrylic acid and acrylic acid are particularly preferred. Y is preferably an acrylate selected from alkyl acrylates and aryl acrylates and preferably selected from (meth) acrylate and alkyl (meth) acrylates wherein the alkyl groups have from 1 to 8 carbon atoms, including, but not limited to, n-butyl

(meth) acrylate, isobutyl (meth) acrylate, methyl (meth) acrylate, and ethyl (meth) acrylate. Preferred E/X/Y-type copolymers are those wherein X is (meth) acrylic acid and/or Y is selected from (meth) acrylate, n-butyl (meth) acrylate, isobutyl (meth) acrylate, methyl (meth) acrylate, and ethyl (meth) acrylate. More preferred E/X/Y-type copolymers are ethylene/(meth) acrylic acid/n-butyl acrylate, ethylene/(meth) acrylic acid/methyl acrylate, and ethylene/(meth) acrylic acid/ethyl acrylate.

[0080] The amount of ethylene in the acid copolymer is typically at least 15 wt. %, preferably at least 25 wt. %, more preferably at least 40 wt. %, and even more preferably at least 60 wt. %, based on total weight of the copolymer. The amount of C₃ to C₈ α,β -ethylenically unsaturated mono- or dicarboxylic acid in the acid copolymer is typically from 1 wt. % to 35 wt. %, preferably from 5 wt. % to 30 wt. %, more preferably from 5 wt. % to 25 wt. %, and even more preferably from 10 wt. % to 20 wt. %, based on total weight of the copolymer. The amount of optional softening comonomer in the acid copolymer is typically from 0 wt. % to 50 wt. %, preferably from 5 wt. % to 40 wt. %, more preferably from 10 wt. % to 35 wt. %, and even more preferably from 20 wt. % to 30 wt. %, based on total weight of the copolymer. "Low acid" and "high acid" ionomeric polymers, as well as blends of such ionomers, may be used. In general, low acid ionomers are considered to be those containing 16 wt. % or less of acid moieties, whereas high acid ionomers are considered to be those containing greater than 16 wt. % of acid moieties.

[0081] The various O/X, E/X, O/X/Y, and E/X/Y-type copolymers are at least partially neutralized with a cation source, optionally in the presence of a high molecular weight organic acid, such as those disclosed in U.S. Pat. No. 6,756,436, the entire disclosure of which is hereby incorporated herein by reference. The acid copolymer can be reacted with the optional high molecular weight organic acid and the cation source simultaneously, or prior to the addition of the cation source. Suitable cation sources include, but are not limited to, metal ion sources, such as compounds of alkali metals, alkaline earth metals, transition metals, and rare earth elements; ammonium salts and monoamine salts; and combinations thereof. Preferred cation sources are compounds of magnesium, sodium, potassium, cesium, calcium, barium, manganese, copper, zinc, lead, tin, aluminum, nickel, chromium, lithium, and rare earth metals. The amount of cation used in the composition is readily determined based on desired level of neutralization. As discussed above, for HNP compositions, the acid groups are neutralized to 70% or greater, preferably 70 to 100%, more preferably 90 to 100%. In one embodiment, an excess amount of neutralizing agent, that is, an amount greater than the stoichiometric amount needed to neutralize the acid groups, may be used. That is, the acid groups may be neutralized to 100% or greater, for example 110% or 120% or greater. In other embodiments, partially-neutralized compositions are prepared, wherein 10% or greater, normally 30% or greater of the acid groups are neutralized. When aluminum is used as the cation source, it is preferably used at low levels with another cation such as zinc, sodium, or lithium, since aluminum has a dramatic effect on melt flow reduction and cannot be used alone at high levels. For example, aluminum is used to neutralize about 10% of the acid groups and sodium is added to neutralize an additional 90% of the acid groups.

[0082] In a particular embodiment, ionomer composition includes an ionomer selected from DuPont® HPF ESX 367, HPF 1000, HPF 2000, HPF AD1035, HPF AD1035 Soft, HPF AD1040, and AD1172 ionomers, commercially available from E. I. du Pont de Nemours and Company. The coefficient of restitution ("COR"), compression, and surface hardness of each of these materials, as measured on 1.55" injection molded spheres aged two weeks at 23° C./50% RH, are given in Table 1 below.

TABLE 1

Example	Solid Sphere COR	Solid Sphere Compression	Solid Sphere Shore D Surface Hardness
HPF 1000	0.830	115	54
HPF 2000	0.860	90	47
HPF AD1035	0.820	63	42
HPF AD1035 Soft	0.780	33	35
HPF AD 1040	0.855	135	60
HPF AD1172	0.800	32	37

[0083] For example, the cover or intermediate layer can be formed from a blend of two or more ionomers. In a particular aspect of this embodiment, the blend is a 50 wt %/50 wt % blend of two different partially-neutralized ethylene/methacrylic acid copolymers.

[0084] In another particular embodiment, the cover or intermediate layer can be formed from a blend of one or more ionomers and a maleic anhydride-grafted non-ionomeric polymer. In a particular aspect of this embodiment, the non-ionomeric polymer is a metallocene-catalyzed polymer. In another particular aspect of this embodiment, the blend includes a partially-neutralized ethylene/methacrylic acid copolymer and a maleic anhydride-grafted metallocene-catalyzed polyethylene.

[0085] In yet another particular embodiment, the cover or intermediate layer can be formed from a composition selected from the group consisting of partially- and fully-neutralized ionomers optionally blended with a maleic anhydride-grafted non-ionomeric polymer; polyester elastomers; polyamide elastomers; and combinations of two or more thereof.

[0086] Ionic plasticizers such as organic acids or salts of organic acids, particularly fatty acids, may be added to the ionomer resin. Such ionic plasticizers are used to make conventional ionomer composition more processable as described in Rajagopalan et al., U.S. Pat. No. 6,756,436, the disclosure of which is hereby incorporated by reference. In the present invention such ionic plasticizers are optional. In one preferred embodiment, a thermoplastic ionomer composition is made by neutralizing about 70 wt % or more of the acid groups without the use of any ionic plasticizer. On the other hand, in some instances, it may be desirable to add a small amount of ionic plasticizer, provided that it does not adversely affect the heat-resistance properties of the composition. For example, the ionic plasticizer may be added in an amount of about 10 to about 50 weight percent (wt. %) of the composition, more preferably 30 to 55 wt. %.

[0087] The organic acids may be aliphatic, mono- or multi-functional (saturated, unsaturated, or multi-unsaturated) organic acids. Salts of these organic acids may also be employed. Suitable fatty acid salts include, for example, metal stearates, laureates, oleates, palmitates, pelargonates, and the like. For example, fatty acid salts such as zinc

stearate, calcium stearate, magnesium stearate, barium stearate, and the like can be used. The salts of fatty acids are generally fatty acids neutralized with metal ions. The metal cation salts provide the cations capable of neutralizing (at varying levels) the carboxylic acid groups of the fatty acids. Examples include the sulfate, carbonate, acetate and hydroxide salts of metals such as barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, or calcium, and blends thereof. It is preferred the organic acids and salts 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).

[0088] Other suitable thermoplastic polymers that may be used to form the cover and intermediate layers include, but are not limited to, the following polymers (including homopolymers, copolymers, and derivatives thereof): (a) polyesters, particularly those modified with a compatibilizing group such as sulfonate or phosphonate, including modified poly(ethylene terephthalate), modified poly(butylene terephthalate), modified poly(propylene terephthalate), modified poly(trimethylene terephthalate), modified poly(ethylene naphthalene), and those disclosed in U.S. Pat. Nos. 6,353,050, 6,274,298, and 6,001,930, the entire disclosures of which are hereby incorporated herein by reference, and blends of two or more thereof; (b) polyamides, polyamide-ethers, and polyamide-esters, and those disclosed in U.S. Pat. Nos. 6,187,864, 6,001,930, and 5,981,654, the entire disclosures of which are hereby incorporated herein by reference, and blends of two or more thereof; (c) polyurethanes, polyureas, polyurethane-polyurea hybrids, and blends of two or more thereof; (d) fluoropolymers, such as those disclosed in U.S. Pat. Nos. 5,691,066, 6,747,110 and 7,009,002, the entire disclosures of which are hereby incorporated herein by reference, and blends of two or more thereof; (e) polystyrenes, such as poly(styrene-co-maleic anhydride), acrylonitrile-butadiene-styrene, poly(styrene sulfonate), polyethylene styrene, and blends of two or more thereof; (f) polyvinyl chlorides and grafted polyvinyl chlorides, and blends of two or more thereof; (g) polycarbonates, blends of polycarbonate/acrylonitrile-butadiene-styrene, blends of polycarbonate/polyurethane, blends of polycarbonate/polyester, and blends of two or more thereof; (h) polyethers, such as polyarylene ethers, polyphenylene oxides, block copolymers of alkenyl aromatics with vinyl aromatics and polyamicesters, and blends of two or more thereof; (i) polyimides, polyetherketones, polyamideimides, and blends of two or more thereof; and (j) polycarbonate/polyester copolymers and blends.

[0089] Core Construction

[0090] As discussed above, the inner core is made preferably from a thermoset rubber composition. In one embodiment, a two-layered or dual-core is made, wherein the inner core is surrounded by an outer core layer. Thermoplastic polymers such as highly-neutralized polymers (HNPs), for example, ethylene acid copolymers containing acid groups, wherein 90% or greater of the acid groups have been neutralized, also can be used.

[0091] Suitable thermoset rubber materials that may be used to form the outer core layer include, but are not limited to, polybutadiene, polyisoprene, ethylene propylene rubber ("EPR"), ethylene-propylene-diene ("EPDM") rubber, styrene-butadiene rubber, styrenic block copolymer rubbers

(such as "SI", "SIS", "SB", "SBS", "SIBS", and the like, where "S" is styrene, "I" is isobutylene, and "B" is butadiene), polyalkenamers such as, for example, polyoctenamer, butyl rubber, halobutyl rubber, polystyrene elastomers, polyethylene elastomers, polyurethane elastomers, polyurea elastomers, metallocene-catalyzed elastomers and plastomers, copolymers of isobutylene and p-alkylstyrene, halogenated copolymers of isobutylene and p-alkylstyrene, copolymers of butadiene with acrylonitrile, polychloroprene, alkyl acrylate rubber, chlorinated isoprene rubber, acrylonitrile chlorinated isoprene rubber, and blends of two or more thereof. Preferably, the outer core layer is formed from a polybutadiene rubber composition.

[0092] The thermoset rubber composition may be cured using conventional curing processes. Suitable curing processes include, for example, peroxide-curing, sulfur-curing, high-energy radiation, and combinations thereof. Preferably, the rubber composition contains a free-radical initiator selected from organic peroxides, high energy radiation sources capable of generating free-radicals, and combinations thereof. In one preferred version, the rubber composition is peroxide-cured. Suitable organic peroxides include, but are not limited to, dicumyl peroxide; n-butyl-4,4-di(t-butylperoxy) valerate; 1,1-di(t-butylperoxy)3,3,5-trimethylcyclohexane; 2,5-dimethyl-2,5-di(t-butylperoxy) hexane; di-t-butyl peroxide; di-t-amyl peroxide; t-butyl peroxide; t-butyl cumyl peroxide; 2,5-dimethyl-2,5-di(t-butylperoxy) hexyne-3; di(2-t-butyl-peroxyisopropyl)benzene; dilauroyl peroxide; dibenzoyl peroxide; t-butyl hydroperoxide; and combinations thereof. In a particular embodiment, the free radical initiator is dicumyl peroxide, including, but not limited to Perkadox® BC, commercially available from Akzo Nobel. Peroxide free-radical initiators are generally present in the rubber composition in an amount of at least 0.05 parts by weight per 100 parts of the total rubber, or an amount within the range having a lower limit of 0.05 parts or 0.1 parts or 1 part or 1.25 parts or 1.5 parts or 2.5 parts or 5 parts by weight per 100 parts of the total rubbers, and an upper limit of 2.5 parts or 3 parts or 5 parts or 6 parts or 10 parts or 15 parts by weight per 100 parts of the total rubber. Concentrations are in parts per hundred (phr) unless otherwise indicated. As used herein, the term, "parts per hundred," also known as "phr" or "pph" is defined as the number of parts by weight of a particular component present in a mixture, relative to 100 parts by weight of the polymer component. Mathematically, this can be expressed as the weight of an ingredient divided by the total weight of the polymer, multiplied by a factor of 100.

[0093] The rubber compositions may further include a reactive cross-linking co-agent. Suitable co-agents include, but are not limited to, metal salts of unsaturated carboxylic acids having from 3 to 8 carbon atoms; unsaturated vinyl compounds and polyfunctional monomers (e.g., trimethylolpropane trimethacrylate); phenylene bismaleimide; and combinations thereof. Particular examples of suitable metal salts include, but are not limited to, one or more metal salts of acrylates, diacrylates, methacrylates, and dimethacrylates, wherein the metal is selected from magnesium, calcium, zinc, aluminum, lithium, and nickel. In a particular embodiment, the co-agent is selected from zinc salts of acrylates, diacrylates, methacrylates, and dimethacrylates. In another particular embodiment, the agent is zinc diacrylate (ZDA). When the co-agent is zinc diacrylate and/or zinc dimethacrylate, the co-agent is typically included in the

rubber composition in an amount within the range having a lower limit of 1 or 5 or 10 or 15 or 19 or 20 parts by weight per 100 parts of the total rubber, and an upper limit of 24 or 25 or 30 or 35 or 40 or 45 or 50 or 60 parts by weight per 100 parts of the base rubber.

[0094] Radical scavengers such as a halogenated organosulfur, organic disulfide, or inorganic disulfide compounds may be added to the rubber composition. These compounds also may function as “soft and fast agents.” As used herein, “soft and fast agent” means any compound or a blend thereof that is capable of making a core: 1) softer (having a lower compression) at a constant “coefficient of restitution” (COR); and/or 2) faster (having a higher COR at equal compression), when compared to a core equivalently prepared without a soft and fast agent. Preferred halogenated organosulfur compounds include, but are not limited to, pentachlorothiophenol (PCTP) and salts of PCTP such as zinc pentachlorothiophenol (ZnPCTP). Using PCTP and ZnPCTP in golf ball inner cores helps produce softer and faster inner cores. The PCTP and ZnPCTP compounds help increase the resiliency and the coefficient of restitution of the core. In a particular embodiment, the soft and fast agent is selected from ZnPCTP, PCTP, ditolyl disulfide, diphenyl disulfide, dixylyl disulfide, 2-nitroresorcinol, and combinations thereof.

[0095] The rubber composition also may include filler(s) such as materials selected from carbon black, clay and nanoclay particles as discussed above, talc (e.g., Luzenac HAR® high aspect ratio talcs, commercially available from Luzenac America, Inc.), glass (e.g., glass flake, milled glass, and microglass), mica and mica-based pigments (e.g., Iriodin® pearl luster pigments, commercially available from The Merck Group), and combinations thereof. Metal fillers such as, for example, particulate; powders; flakes; and fibers of copper, steel, brass, tungsten, titanium, aluminum, magnesium, molybdenum, cobalt, nickel, iron, lead, tin, zinc, barium, bismuth, bronze, silver, gold, and platinum, and alloys and combinations thereof also may be added to the rubber composition to adjust the specific gravity of the composition as needed. In addition, the rubber compositions may include antioxidants. Also, processing aids such as high molecular weight organic acids and salts thereof may be added to the composition. Suitable organic acids are aliphatic organic acids, aromatic organic acids, saturated mono-functional organic acids, unsaturated monofunctional organic acids, multi-unsaturated mono-functional organic acids, and dimerized derivatives thereof. Particular examples of suitable organic acids include, but are not limited to, caproic acid, caprylic acid, capric acid, lauric acid, stearic acid, behenic acid, erucic acid, oleic acid, linoleic acid, myristic acid, benzoic acid, palmitic acid, phenylacetic acid, naphthalenoic acid, and dimerized derivatives thereof. The organic acids are aliphatic, mono-functional (saturated, unsaturated, or multi-unsaturated) organic acids. Salts of these organic acids may also be employed. The salts of organic acids include the salts of barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, or calcium, salts of fatty acids, particularly stearic, behenic, erucic, oleic, linoleic or dimerized derivatives thereof. It is preferred that the organic acids and salts of the present invention be relatively non-migratory (they do not bloom to the surface of the polymer under ambient temperatures) and non-volatile

(they do not volatilize at temperatures required for melt-blending.) Other ingredients such as accelerators (for example, tetra methylthiuram), processing aids, dyes and pigments, wetting agents, surfactants, plasticizers, coloring agents, fluorescent agents, chemical blowing and foaming agents, defoaming agents, stabilizers, softening agents, impact modifiers, antiozonants, as well as other additives known in the art may be added to the rubber composition.

[0096] Examples of commercially-available polybutadiene rubbers that can be used in accordance with this invention, include, but are not limited to, BR 01 and BR 1220, available from BST Elastomers of Bangkok, Thailand; SE BR 1220LA and SE BR1203, available from DOW Chemical Co of Midland, Mich.; BUDENE 1207, 1207s, 1208, and 1280 available from Goodyear, Inc of Akron, Ohio; BR 01, 51 and 730, available from Japan Synthetic Rubber (JSR) of Tokyo, Japan; BUNA CB 21, CB 22, CB 23, CB 24, CB 25, CB 29 MES, CB 60, CB Nd 60, CB 55 NF, CB 70 B, CB KA 8967, and CB 1221, available from Lanxess Corp. of Pittsburgh, Pa.; BR1208, available from LG Chemical of Seoul, South Korea; UBEPOL BR130B, BR150, BR150B, BR150L, BR230, BR360L, BR710, and VCR617, available from UBE Industries, Ltd. of Tokyo, Japan; EUROPRENE NEOCIS BR 60, INTENE 60 AF and P30AF, and EUROPRENE BR HV80, available from Polimeri Europa of Rome, Italy; AFDENE 50 and NEODENE BR40, BR45, BR50 and BR60, available from Karbochem (PTY) Ltd. of Bruma, South Africa; KBR 01, NdBr 40, NdBR-45, NdBr 60, KBR 710S, KBR 710H, and KBR 750, available from Kumho Petrochemical Co., Ltd. Of Seoul, South Korea; and DIENE 55NF, 70AC, and 320 AC, available from Firestone Polymers of Akron, Ohio.

[0097] In one embodiment, as discussed above, the core composition comprises polybutadiene rubber, zinc diacrylate, zinc oxide, stearic acid and/or zinc stearate, a filler such as barium sulfate, a peroxide or other cross-linking initiator, and optionally an organosulfur compound such as zinc pentachlorothiophenol (PCTP), and optionally an antioxidant, and colorant pigment or dye. The ingredients are mixed in an internal mixer such a Farrell Intermix mixer, two-roll mill, or any other suitable mixer for mixing rubber. The order of addition of ingredients and the time and temperature of mixing are important. Generally, the rubber and all ingredients (except peroxide) are mixed from about 1 to 30 minutes, and more preferably about 2 to 10 minutes at a temperature of about room temperature to about 200° F. The heat-sensitive peroxide initiator is added at a temperature of about 210° F. or less, preferably about 200° F. or less and mixed for a period of time that ensures good dispersion and uniform mixing of all ingredients. The temperature of the batch should not rise above the decomposition temperature of the peroxide, generally not exceeding 220° F., more preferably not above 210° F., whereupon the batch is discharged from the mixer onto a two-roll mill or a twin-screw sheeter or other device that allows the batch to cool for storage and testing prior to subsequent processing into preforms (generally, extrusion or barwell) and then molding. Alternatively, the subsequent processing steps of extrusion and molding may take place directly upon removal from the mixer, while the batch is still warm.

Test Methods

[0098] Test Methods

[0099] Hardness.

[0100] 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.

[0101] 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 sub-assembly is centered under the durometer indenter before a surface hardness reading is obtained. A calibrated, digital durometer, capable of reading to 0.1 hardness units is used for the hardness measurements. The digital durometer must be attached to, and its foot made parallel to, the base of an automatic stand. The weight on the durometer and attack rate conforms to ASTM D-2240.

[0102] In certain embodiments, a point or plurality of points measured along the "positive" or "negative" gradients may be above or below a line fit through the gradient and its outermost and innermost hardness values. In an alternative

preferred embodiment, the hardest point along a particular steep "positive" or "negative" gradient may be higher than the value at the innermost portion of the inner core (the geometric center) or outer core layer (the inner surface)—as long as the outermost point (i.e., the outer surface of the inner core) is greater than (for "positive") or lower than (for "negative") the innermost point (i.e., the geometric center of the inner core or the inner surface of the outer core layer), such that the "positive" and "negative" gradients remain intact.

[0103] As discussed above, the direction of the hardness gradient of a golf ball layer is defined by the difference in hardness measurements taken at the outer and inner surfaces of a particular layer. The center hardness of an inner core and hardness of the outer surface of an inner core in a single-core ball or outer core layer are readily determined according to the test procedures provided above. The outer surface of the inner core layer (or other optional intermediate core layers) in a dual-core ball are also readily determined according to the procedures given herein for measuring the outer surface hardness of a golf ball layer, if the measurement is made prior to surrounding the layer with an additional core layer. Once an additional core layer surrounds a layer of interest, the hardness of the inner and outer surfaces of any inner or intermediate layers can be difficult to determine. Therefore, for purposes of the present invention, when the hardness of the inner or outer surface of a core layer is needed after the inner layer has been surrounded with another core layer, the test procedure described above for measuring a point located 1 mm from an interface is used. Likewise, the midpoint of a core layer is taken at a point equidistant from the inner surface and outer surface of the layer to be measured, most typically an outer core layer. Once again, when one or more core layers surround a layer of interest, the exact midpoint may be difficult to determine, therefore, for the purposes of the present invention, the measurement of "midpoint" hardness of a layer is taken within plus or minus 1 mm of the measured midpoint of the layer.

[0104] Also, it should be understood that there is a fundamental difference between "material hardness" and "hardness as measured directly on a golf ball." For purposes of the present invention, material hardness is measured according to ASTM D2240 and generally involves measuring the hardness of a flat "slab" or "button" formed of the material. Surface hardness as measured directly on a golf ball (or other spherical surface) typically results in a different hardness value. The difference in "surface hardness" and "material hardness" values is due to several factors including, but not limited to, ball construction (that is, core type, number of cores and/or cover layers, and the like); ball (or sphere) diameter; and the material composition of adjacent layers. It also should be understood that the two measurement techniques are not linearly related and, therefore, one hardness value cannot easily be correlated to the other. Shore hardness (for example, Shore C or Shore D hardness) was measured according to the test method ASTM D-2240.

[0105] Compression.

[0106] As disclosed in Jeff Dalton's Compression by Any Other Name, Science and Golf IV, Proceedings of the World Scientific Congress of Golf (Eric Thain ed., Routledge, 2002) ("J. Dalton"), several different methods can be used to measure compression, including Atti compression, Riehle compression, load/deflection measurements at a variety of fixed loads and offsets, and effective modulus. For purposes

of the present invention, compression refers to Soft Center Deflection Index (“SCDI”). The SCDI is a program change for the Dynamic Compression Machine (“DCM”) that allows determination of the pounds required to deflect a core 10% of its diameter. The DCM is an apparatus that applies a load to a core or ball and measures the number of inches the core or ball is deflected at measured loads. A crude load/deflection curve is generated that is fit to the Atti compression scale that results in a number being generated that represents an Atti compression. The DCM does this via a load cell attached to the bottom of a hydraulic cylinder that is triggered pneumatically at a fixed rate (typically about 1.0 ft/s) towards a stationary core. Attached to the cylinder is an LVDT that measures the distance the cylinder travels during the testing timeframe. A software-based logarithmic algorithm ensures that measurements are not taken until at least five successive increases in load are detected during the initial phase of the test. The SCDI is a slight variation of this set up. The hardware is the same, but the software and output has changed. With the SCDI, the interest is in the pounds of force required to deflect a core x amount of inches. That amount of deflection is 10% percent of the core diameter. The DCM is triggered, the cylinder deflects the core by 10% of its diameter, and the DCM reports back the pounds of force required (as measured from the attached load cell) to deflect the core by that amount. The value displayed is a single number in units of pounds.

[0107] Coefficient of Restitution (“COR”).

[0108] The COR is determined according to a known procedure, wherein a golf ball or golf ball sub-assembly (for example, a golf ball core) is fired from an air cannon at two given velocities and a velocity of 125 ft/s is used for the calculations. Ballistic light screens are located between the air cannon and steel plate at a fixed distance to measure ball velocity. As the ball travels toward the steel plate, it activates each light screen and the ball’s time period at each light screen is measured. This provides an incoming transit time period which is inversely proportional to the ball’s incoming velocity. The ball makes impact with the steel plate and rebounds so it passes again through the light screens. As the rebounding ball activates each light screen, the ball’s time period at each screen is measured. This provides an outgoing transit time period which is inversely proportional to the ball’s outgoing velocity. The COR is then calculated as the ratio of the ball’s outgoing transit time period to the ball’s incoming transit time period ($COR = V_{out}/V_{in} = T_{in}/T_{out}$).

[0109] When numerical lower limits and numerical upper limits are set forth herein, it is contemplated that any combination of these values may be used. Other than in the operating examples, or unless otherwise expressly specified, all of the numerical ranges, amounts, values and percentages such as those for amounts of materials and others in the specification may be read as if prefaced by the word “about” even though the term “about” may not expressly appear with the value, amount or range. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention.

[0110] All patents, publications, test procedures, and other references cited herein, including priority documents, are fully incorporated by reference to the extent such disclosure is not inconsistent with this invention and for all jurisdictions in which such incorporation is permitted.

[0111] It is understood that the compositions and golf ball products described and illustrated herein represent only some embodiments of the invention. It is appreciated by those skilled in the art that various changes and additions can be made to compositions and products without departing from the spirit and scope of this invention. It is intended that all such embodiments be covered by the appended claims.

1. A method for making a multi-piece golf ball, comprising the steps of:

- a) introducing a first composition comprising Compound A into upper and lower mold members, the upper and lower mold members defining a mold cavity with a dimple pattern;
- b) introducing a second composition comprising Compound B into the upper and lower mold members so that the first and second compositions are mixed together to form a heterogeneous composition comprising Compounds A and B;
- c) placing a spherical core into the mold cavity;
- d) applying heat and pressure to the mold members so the heterogeneous composition encapsulates the core and forms an outer cover having a dimpled pattern, and e) removing the multi-piece golf ball from the mold.

2. The method of claim 1, wherein Compound A is an aliphatic polyurethane and Compound B is an aromatic polyurethane.

3. The method of claim 1, wherein Compound A and Compound B are O/X-type copolymers, wherein O is selected from the group consisting of ethylene and propylene, and X is an acid group selected from the group consisting of methacrylic acid, acrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid, and itaconic acid, and wherein at least 70% of the acid groups in Compound A are neutralized, and greater than 70% of the acid groups in Compound B are neutralized.

4. The method of claim 3, wherein the O of the O/X-type acid copolymer is ethylene and the X is methacrylic acid or acrylic acid.

5. The method of claim 1, wherein Compound A and Compound B are O/X/Y-type copolymers, wherein O is selected from the group consisting of ethylene and propylene, and X is an acid group selected from the group consisting of methacrylic acid, acrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid, and itaconic acid, and Y is a (meth) acrylate or alkyl (meth) acrylate wherein the alkyl groups have from 1 to 8 carbon atoms, and wherein at least 70% of the acid groups in Compound A are neutralized, and greater than 70% of the acid groups in Compound B are neutralized.

6. The method of claim 1, wherein the outer cover layer formed from the heterogeneous composition has a midpoint hardness and outer hardness surface, the hardness of the outer surface being greater than the hardness of the midpoint to define a positive hardness gradient.

7. The method of claim 1, wherein the hardness of the outer surface is in the range of about 35 to about 90 Shore D and the hardness of the midpoint is in the range of about 30 to about 80 Shore D.

8. The golf ball of claim 1, wherein the outer cover layer formed from the heterogeneous composition has a midpoint hardness and outer hardness surface, the hardness of the outer surface being the same or greater than the hardness of the midpoint to define a zero or negative hardness gradient.

9. The method of claim 8, wherein the hardness of the midpoint is in the range of about 40 to about 75 Shore D and the hardness of the outer surface is in the range of about 35 to about 70 Shore D.

10. The method of claim 1, wherein the core is single-layered, the core being formed from a rubber composition.

11. The method of claim 1, wherein the core is dual-layered, the core comprising an inner core and surrounding outer core layer, at least one of the core layers being formed from a rubber composition.

12. A method for making a multi-piece golf ball, comprising the steps of:

- a) introducing a first composition comprising Compound A into upper and lower mold members, the upper and lower mold members defining a mold cavity;
- b) introducing a second composition comprising Compound B into the upper and lower mold members so that the first and second compositions are mixed together to form a heterogeneous composition comprising Compounds A and B;
- c) placing a spherical core into the mold cavity;
- d) applying heat and pressure to the mold members so the heterogeneous composition encapsulates the core and forms an intermediate layer the core and surrounding intermediate layer comprising a ball subassembly;
- e) removing the ball subassembly from the mold; and
- f) forming a cover having at least one layer over the subassembly to form a multi-piece golf ball.

* * * * *