GOLF BALLS WITH IMPROVED FEEL

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ABSTRACT
A golf ball including a polyurethane cover layer, a solid core, and one or more intermediate layers, and wherein the ball has a Sound Pressure Level, S, of less than 81.5 dB. In a further embodiment there is a golf ball including a polyurethane cover layer, a solid core, and one or more intermediate layers, and wherein the ball has a Sound Pressure Level, S, of less than 81.5 dB and wherein S meets the following inequality;

\[ S < 0.032143F + 189.5 \]

where \( F \) is the golf ball frequency in Hz. In an additional embodiment disclosed is a golf ball including a polyurethane cover layer, a solid core, and one or more intermediate layers, and wherein the ball has a Sound Pressure Level, S, of less than 81.5 dB and wherein S meets the following inequality;

\[ S < 0.01F + 112 \]

where \( F \) is the golf ball frequency in Hz. In another embodiment disclosed is a golf ball including a polyurethane cover layer, a solid core, and one or more intermediate layers, and wherein the ball has a Sound Pressure Level, S, of less than 81.5 dB and wherein S meets the following inequality;

\[ S < 0.01F + 112 \]

where \( F \) is the golf ball frequency in Hz, and wherein the polyurethane cover includes a thermoset polyurethane.
GOLF BALLS WITH IMPROVED FEEL

CROSS REFERENCE TO RELATED APPLICATION
[0001] This application claims the benefit of U.S. Provisional Application No. 60/878,024, filed Dec. 29, 2006, which is incorporated herein by reference in its entirety.

FIELD
[0002] Disclosed herein are multilayered golf ball having a solid core, a multilayered construction and a polyurethane cover, and which, when struck by the golfer generates a sound of a specific frequency and loudness.

BACKGROUND
[0003] The application of synthetic polymer chemistry to the field of sports equipment has revolutionized the performance of athletes in many sports. One sport in which this is particularly true is golf, especially as relates to advances in golf ball performance and ease of manufacture. For instance, the earliest golf balls consisted of a leather cover filled with wet feathers. These “featherly” golf balls were subsequently replaced with a single piece golf ball made from “gutta percha,” a naturally occurring rubber-like material.

[0004] More recently wound balls typically have either a solid rubber or liquid filled center around which many yards of a stretched elastic thread or yarns are wound to form a core. The wound core is then covered with a durable cover material such as an ionomer or other thermoplastic material or a softer cover such as balata or cast polyurethane. Wound balls are generally soft and provide more spin, which enables a skilled golfer to have more control over the ball’s flight. In particular, it is desirable that a golfer be able to impart backspin to a golf ball for purposes of controlling its flight and controlling the action of the ball upon landing on the ground. For example, substantial backspin will make the ball stop once it strikes the landing surface instead of bounding forward. The ability to impart backspin onto a golf ball is related to the extent to which the golf ball cover deforms when it is struck with a golf club. Because wound balls are traditionally more deformable than conventional two-piece balls, it is easier to impart spin to wound balls. However, wound higher spinning balls typically travel a shorter distance when struck as compared to a two-piece ball. Moreover, as a result of their more complex structure, wound balls generally require a longer time to manufacture and are more expensive to produce than a two-piece ball.

[0005] Golf balls having a two-piece construction generally are most popular with the recreational golfer, because they are relatively durable and provide increased distance as compared to a typical wound ball with a balata cover. Two-piece balls have a single solid core, usually formed of a cross-linked rubber, which is encased by a cover. Typically, the solid core is made of polybutadiene, which is chemically cross-linked with peroxide, or sulfur compounds together with co-cross-linking agent, such as zinc diacrylate.

The cover of such balls often comprises tough, cut-proof blends of one or more materials known as ionomers, which typically are ethylene/acyrlic acid copolymers or ethylene/acyrlic acid/acyrlic terpolymers in which some or all of the acid groups are neutralized with metal cations. Such ionomers are commercially available under trademarks such as SURLYN®, which is sold commercially by E.I. DuPont de Nemours & Company, of Wilmington, Del., or JOTEK® which is sold commercially by ExxonMobil, of Irving, Tex.

SUMMARY
[0006] In one embodiment, the golf ball includes a polyurethane cover layer, a solid core, and one or more intermediate layers, and wherein the ball has a Sound Pressure Level, $S$, of less than 81.5 dB.

[0007] In a further embodiment the golf ball includes a polyurethane cover layer, a solid core, and one or more intermediate layers, and wherein the ball has a Sound Pressure Level, $S$, of less than 81.5 dB and wherein $S$ meets the following inequality;

$$S < 0.032143F + 189.5;$$

where $F$ is the golf ball frequency in Hz.

[0008] In a further embodiment the golf ball includes a polyurethane cover layer, a solid core, and one or more intermediate layers, and wherein the ball has a Sound Pressure Level, $S$, of less than 81.5 dB and wherein $S$ meets the following inequality;

$$S < 0.01F + 112;$$

where $F$ is the golf ball frequency in Hz.

[0009] In a further embodiment the golf ball includes a polyurethane cover layer, a solid core, and one or more intermediate layers, and wherein the ball has a Sound Pressure Level, $S$, of less than 81.5 dB and wherein $S$ meets the following inequality;

$$S < 0.01F + 112;$$

where $F$ is the golf ball frequency in Hz, and wherein the polyurethane cover includes a thermoset polyurethane.

[0010] In a further embodiment the golf ball includes a cover layer, a core, and one or more intermediate layers, and wherein the ball has a solid core; a cover comprising polyurethane, polyurea or a combination thereof; and a Sound Pressure Level, $S$, of less than 81 dB.

[0011] In a further embodiment the golf ball includes a cover layer, a core, and one or more intermediate layers, and wherein the ball has a solid core; and a thermoset polyurethane; wherein the golf ball has a golf ball frequency of $\leq 3360$ Hz.

[0012] In a further embodiment the golf ball includes a cover layer, a core, and one or more intermediate layers, and wherein the ball has a solid core; and a polyurethane cover or polyurea cover; wherein the golf ball has a golf ball frequency of $< 3360$ Hz.

BRIEF DESCRIPTION OF DRAWINGS
[0013] FIG. 1 illustrates a three-piece golf ball 1 comprising a solid center or core 2, an intermediate layer 3, and an outer cover layer 4.

[0014] FIG. 2 illustrates a 4-piece golf ball 1 comprising a core 2, and an outer cover layer 5 an inner intermediate layer 3, and an outer intermediate layer 4.

[0015] Although FIGS. 1 and 2 illustrate only three- and four-piece golf ball constructions, golf balls may comprise from 1 to at least 5 intermediate layer(s), preferably from 1 to 3 intermediate layer(s), more preferably from 1 to 2 intermediate layer(s).

DETAILED DESCRIPTION
[0016] The following definitions are provided to aid the reader, and are not intended to provide term definitions that would be narrower than would be understood by a person of ordinary skill in the art of golf ball composition and manufacture.
Any numerical values recited herein include all values from the lower value to the upper value. All possible combinations of numerical values between the lowest value and the highest value enumerated herein are expressly included in this application. The term “bimodal polymer” refers to a polymer comprising two main fractions and more specifically to the form of the polymer’s molecular weight distribution curve, i.e., the appearance of the graph of the polymer weight fraction as a function of its molecular weight. When the molecular weight distribution curve for these fractions is superimposed onto the molecular weight distribution curve for the total resulting polymer product, that curve will show two maxima or at least be distinctly broadened in comparison with the curves for the individual fractions. Such a polymer product is called bimodal. The chemical compositions of the two fractions may be different. The term “chain extender” as used herein is a compound added to either polyurethane or polyurea prepolymer, or the prepolymer starting materials, which undergoes additional reaction but at a level sufficiently low to maintain the thermoplastic properties of the final composition. The term “conjugated” refers to an organic compound containing two or more sites of unsaturation (e.g., carbon-carbon double bonds, carbon-carbon triple bonds, and sites of unsaturation comprising atoms other than carbon, such as nitrogen) separated by a single bond. The term “curing agent” or “curing system” as used interchangeably herein is a compound added to either polyurethane or polyurea prepolymer, or the prepolymer starting materials, which imparts additional crosslinking to the final composition to render it a thermoset. As used herein, the term “core” is intended to mean the elastic center of a golf ball, which may have a unitary construction. Alternatively the core itself may have a layered construction, e.g., having a spherical “center” and additional “core layers,” with such layers being made of the same material or a different material from the core center. The term “cover” is meant to include any layer of a golf ball that surrounds the core. Thus a golf ball cover may include both the outermost layer and also any intermediate layers, which are disposed between the golf ball center and outer cover layer. “Cover” may be used interchangeably with the term “cover layer”. A “fibrer” is a general term and the definition provided by Engineered Materials Handbook, Vol. 2, “Engineering Plastics”, published by A.S.M. International, Metals Park, Ohio, USA, is relied upon to refer to filamentary materials with a finite length that is at least 100 times its diameter, which typically is 0.10 to 0.13 mm (0.004 to 0.005 in.). Fibers can be continuous or specific short lengths (discontinuous), normally no less than 3.2 mm (⅝ in.). Although fibers according to this definition are preferred, fiber segments, i.e., parts of fibers having lengths less than the aforementioned also may be used in the present invention. Embodiments of the golf ball components described herein may include fibers including, by way of example and without limitation, glass fibers, such as E fibers, Cem-Fil filament fibers, and 204 filament strand fibers; carbon fibers, such as graphite fibers, high modulus carbon fibers, and high strength carbon fibers; asbestos fibers, such as chrysotile and crocidolite; cellulose fibers; aramid fibers, such as Kevlar, including types PRD 29 and PRD 49; and metallic fibers, such as copper, high tensile steel, and stainless steel. In addition, single crystal fibers, potassium titrate fibers, calcium sulphate fibers, and fibers or filaments of one or more linear synthetic polymers, such as Terylene, Dacron, Perlon, Orion, Nylon, including Nylon type 242, are contemplated. Polypropylene fibers, including monofilament and fibrillated fibers are also contemplated. Golf balls according to the present invention also can include any combination of such fibers. Fibers used in golf ball components are described more fully in Kim et al., U.S. Pat. No. 6,012,991, which is incorporated herein by reference. In the case of a ball with two intermediate layers, the term “inner intermediate layer” may be used interchangeably herein with the terms “inner mantle” or “inner mantle layer” and is intended to mean the intermediate layer of the ball positioned nearest to the core. The term “intermediate layer” may be used interchangeably with “mantle layer,” “inner cover layer” or “inner cover” and is intended to mean any layer(s) in a golf ball disposed between the core and the outer cover layer. The term “(meth)acrylate” is intended to mean an ester of methacrylic acid and/or acrylic acid. The term “(meth)acrylic acid copolymers” is intended to mean copolymers of methacrylic acid and/or acrylic acid. A “nanofiller” is defined as a material having an aggregate structure with the aggregate particle sizes in the micron range and above. However, these aggregates have a stacked plate structure with the individual platelets being roughly from about 1 nanometer (nm) thick and from about 100 to about 1000 nm across. As a result, nanofillers have extremely high surface area, resulting in high reinforcement efficiency to the material at low loading levels of the particles. Typically such sub-micron-sized particles enhance the stiffness of the material, without increasing its weight or opacity and without reducing the material’s low-temperature toughness. Inorganic nanofiller materials generally are made from clay, and to facilitate incorporation of the nanofiller material into the polymer material, either in preparing nanocomposite materials or in preparing polymer-based golf ball compositions, the clay particles generally are coated or treated by a suitable compatibilizing agent or coupling agent as described below. A “nanocomposite” is defined as a polymer matrix having nanofiller within the matrix. Nanocomposite materials and golf balls made comprising nanocomposite materials are disclosed in Kim et al., U.S. Pat. No. 6,794,447, and US Patent Publication No. 2005/0057956 A1, as well as U.S. Pat. No. 5,962,553 to Ellsworth, U.S. Pat No. 5,385,776 to Maxfield et al., and U.S. Pat. No. 4,894,411 to Okada et al., the disclosure of each of which are incorporated herein by reference in their entirety. Examples of nanocomposite materials currently marketed include M1030D, manufactured by Unitika Limited, of Osaka, Japan, and J105C2, manufactured by UBE America of New York, N.Y. The term “outer cover layer” is intended to mean the outermost cover layer of the golf ball on which, for example, the dimple pattern, paint and any writing, symbol, etc. is placed. If, in addition to the core, a golf ball comprises two or more cover layers, only the outermost layer is designated the outer cover layer. The remaining layers may be designated intermediate layers. The term outer cover layer is interchangeable with the term “outer cover”. In the case of a ball with two intermediate layers, the term “outer intermediate layer” may be used interchangeably herein with the terms “outer mantle” or “outer mantle layer”
and is intended to mean the intermediate layer of the ball which is disposed nearest to the outer cover layer.

“Peptizers” are chemical(s) or compositions that have been used by rubber compounders to facilitate the processing of natural or synthetic rubbers and other difficult-to-process high viscosity elastomers during milling and mastication.

The term “polynol” is used interchangeably herein with the term “polynol rubber” and means a polymer of one or more alkenes, including cycloalkenes, having from 5-20, preferably 5-15, most preferably 5-12 ring carbon atoms. The polynolamers may be prepared by any suitable method including ring opening metathesis polymerization of one or more cycloalkenes in the presence of organometallic catalysts as described in U.S. Pat. Nos. 3,492,245, and 3,804,803, the entire contents of both of which are incorporated herein by reference.

“Prepolymer” refers to any material that can be further processed to form a final polymer material of a manufactured golf ball such as, by way of example and not limitation, a polymerized or partially polymerized material that can undergo additional processing, such as crosslinking.

The term “polyurea” as used herein refers to materials prepared by reaction of a diisocyanate with a polyamine.

The term “polyurethane” as used herein refers to materials prepared by reaction of a diisocyanate with a polyl.

A “thermoplastic” is generally defined as a material that is capable of softening or melting when heated and of hardening again when cooled. Thermoplastic polymer chains often are not cross-linked or are lightly cross-linked using a chain extender, but the term “thermoplastic” as used herein may refer to materials that initially act as thermoplastics, such as during an initial extrusion process or injection molding process, but which also may be crosslinked, such as during a compression molding step to form a final structure.

A “thermoset” is generally defined as a material that crosslinks or cures via interaction with a crosslinking or curing agent. The crosslinking may be brought about by energy in the form of heat (generally above 200 degrees Celsius), through a chemical reaction (by reaction with a curing agent), or by irradiation. The resulting composition remains rigid when set, and does not soften with heating. Thermosets have this property because the long-chain polymer molecules cross-link with each other to give a rigid structure. A thermoset material cannot be melted and re-molded after it is cured thus thermosets do not lend themselves to recycling unlike thermoplastics, which can be melted and re-molded.

The term “thermoplastic polyurethane” refers to a material prepared by reaction of a prepared by reaction of a diisocyanate with a polyl, and optionally addition of a chain extender.

The term “thermoplastic polyurea” refers to a material prepared by reaction of a prepared by reaction of a diisocyanate with a polyamine, with optionally addition of a chain extender.

The term “thermoset polyurea” refers to a material prepared by reaction of a diisocyanate with a polyl, and a curing agent.

The term “thermoset polyurethane” refers to a material prepared by reaction of a diisocyanate with a polyamine, and a curing agent.

A “urethane prepolymer” is the reaction product of diisocyanate and a polyl.

A “urea prepolymer” is the reaction product of a diisocyanate and a polyamine.

The term “unimodal polymer” refers to a polymer comprising one main fraction and more specifically to the form of the polymer’s molecular weight distribution curve, i.e., the molecular weight distribution curve for the total polymer product shows only a single maximum.

The combination of the above-described core and cover materials provides a “hard” covered ball that is resistant to cutting and other damage caused by striking the ball with a golf club. Further, such a combination imparts a high initial velocity to the ball, which results in increased distance. Due to their hardness, however, these two-piece balls have a relatively low spin rate, which makes them difficult to control, particularly on relatively short approach shots. As such, these balls generally are considered to be “distance” balls. Because the materials of two-piece balls are very rigid, the balls typically have a hard “feel” when struck by a club. The feel of a golf ball is the perception of how the impact of the club on a golf ball is perceived by the striker and represents a combination of both the hardness or softness of the ball but also and primarily the sound of the impact experienced by the striker.

Frequency is a measure of the “pitch” of the sound, and true loudness is measured in decibel (db) levels. Balls can be hit or tested at 30 yard shots for sound and pitch and subsequently this translates into ball feel that the golfer experiences. Urethane is a soft, material but relatively low in rebound so ball manufacturers have had to compensate for this by combining such covers with cores high in compression or firmer or harder, coupled with mantle layers also firmer and harder, both of which maintain ball speed but increases feel. By plotting db levels v. frequency, you obtain a ratio of “feel”. Earlier wound balata balls have a very low ratio, and subsequently low or soft feel. Firm two piece distance balls have a high ratio, i.e. they are very firm and have a loud feel. To date, multilayered balls with a urethane cover and a solid core have not been made near the feel ratio of previous tour balata balls. This invention creates golf balls with ratios softer than what exists today, bringing back the feel of the wound balls while using a urethane cover.

More recently, a number of golf ball manufacturers have introduced multi-layer golf balls, i.e., having at least a core, intermediate layer or mantle, and one or more cover layers, in an effort to overcome some of the undesirable aspects of conventional two-piece balls, such as their hard feel. In attempts to further modify the ball performance, especially in terms of the distance such balls travel, and the feel transmitted to the golfer through the club on striking the ball, the basic two piece ball construction has been further modified by the introduction of additional layers between the core and outer cover layer. If one additional layer is introduced between the core and outer cover layer, a so-called “three-piece ball” results, and similarly, if two additional layers are introduced between the core and outer cover layer, a so-called “four-piece ball” results, and so on. Such a multi-layer structure allows the introduction of new materials of varying hardness and whereby deficiencies in a property in one layer may be mitigated by the introduction of a different material in another. At the present time, SURLYN® is used as the primary source of cover stock for most multilayer three-piece golf balls. The problem with SURLYN®-covered golf balls, however, is that they lack the “click” and “feel” which golfers had become accustomed to with balata. “Click” is the sound
made when the ball is hit by a golf club while “feel” is the overall sensation imparted to the golfer when the ball is hit. Unlike SURLYN®-covered golf balls, polyurethane-covered golf balls can be made to have the “click” and “feel” of balata but with increased durability. Polyurethanes or polyureas are typically prepared by the reaction of a diisocyanate with a polyol (in the case of polyurethanes) or with a polyamine (in the case of a polyurea). Thermoplastic polyurethanes or polyureas may consist solely of this initial mixture or may be further combined with a chain extender to vary properties such as hardness of the thermoplastic. Thermoset polyurethanes or polyureas typically are formed by the reaction of a diisocyanate and a polyol or polyamine respectively, and an additional crosslinking agent to crosslink or cure the material to result in a thermoset. Thus, multilayered golf balls with a solid core and a polyurethane cover have become ubiquitous in usage by professional golfers on the various professional tours throughout the world.

However, since their introduction, ball compressions have increased with the search for more distance and the overall short game feel has been sacrificed. Players have accepted this firmer feel due to the increase in distance. Disclosed herein are solid cored multilayered polyurethane covered golf balls having a specific sound frequency and loudness which creates softer overall sound/feel, like those of balata balls of the past, with improved speed, and distance over the wound balls of the past. The present invention can be used to form golf balls of any desired size. “The Rules of Golf” by the USGA dictate that the size of a competition golf ball must be at least 1.680 inches in diameter; however, golf balls of any size can be used for leisure golf play. The preferred diameter of the golf balls is from about 1.670 inches to about 1.800 inches. Oversize golf balls with diameters above about 1.760 inches to as big as 2.75 inches also are within the scope of the invention.

Any isocyanate available to one of ordinary skill in the art is suitable for use in the disclosed golf balls. Isocyanates include, but are not limited to, aliphatic, cycloaliphatic, aromatic aliphatic, aromatic, any derivatives thereof, and combinations of these compounds having two or more isocyanate (NCO) groups per molecule. As used herein, aromatic aliphatic compounds should be understood as those containing an aromatic ring, wherein the isocyanate group is not directly bonded to the ring. One example of an aromatic aliphatic compound is a tetramethylene disocyanate (TMXDI). The isocyanates may be organic isocyanateterminated prepolymers, low free isocyanate prepolymer, and mixtures thereof. The isocyanate-containing reactable component may also include any isocyanate-functional monomer, dimer, trimer, or polymeric adduct thereof, prepolymer, quasi-prepolymer, or mixtures thereof. Isocyanate-functional compounds may include monoisocyanates or polyisocyanates that include any isocyanate functionality of two or more.

Suitable isocyanate-containing components include diisocyanates having the generic structure: 

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\text{OC} = \text{N} - \text{R} - \text{N} = \text{C} - \text{O}, \text{ where R is preferably a cyclic, aromatic, or linear or branched hydrocarbon moiety containing from about 1 to about 50 carbon atoms. The isocyanate may also contain one or more cyclic groups or one or more phenyl groups. When multiple cyclic or aromatic groups are present, linear and/or branched hydrocarbons containing from about 1 to about 50 carbon atoms can be present as spacers between the cyclic or aromatic groups. In some cases, the cyclic or aromatic group(s) may be substituted at the 2-, 3-, and/or 4-positions, or at the ortho-, meta-, and/or para-positions, respectively. Substituted groups may include, but are not limited to, halogens, primary, secondary, or tertiary hydrocarbon groups, or a mixture thereof.}
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diisocyanate, 2,4-chlorophenylene diisocyanate, 4,4'-diphenylmethane diisocyanate, p,p'-diphenylmethane diisocyanate, 2,4-tolyene diisocyanate, 2,6-tolyene diisocyanate, 2,2'-diphenylpropane-4,4'-diisocyanate, 4,4'-toluidine diisocyanate, diphenylene diisocyanate, 1,3-xylene diisocyanate, 1,4-naphthylene diisocyanate, azobenzene-4,4'-diisocyanate, diphenyl sulfone-4,4'-diisocyanate, triphenylmethane 4,4',4'-trisocyanate, isocyanatoethyl methacrylate, 3-isopropenyl-ω,ω,ω-trimethyl-1-isocyanate, dichlorohexamethylene diisocyanate, ω,ω'-diisocyanato-1,4-diethylbenzene, polyethylene polyphenylene polyisocyanate, isocyanurated modified compounds, and carbodiimide modified compounds, as well as biuret modified compounds of the above polysocyanates. These isocyanates may be used either alone or in combination. These combination isocyanates include triisocyanates, such as biuret of hexamethylene diisocyanate and triphenylmethane triisocyanates, and polysocyanates, such as polymeric diphenylmethane diisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate (TMDI); 4,4'-dicyclohexylmethane diisocyanate (H₂MDI); 2,4-hexahydrotoluene diisocyanate; 2,6-hexahydrotoluene diisocyanate; 1,2-, 1,3-, and 1,4-phenylene diisocyanate; aromatic aliphatic isocyanate, such as 1,2-, 1,3-, and 1,4-xylene diisocyanate; meta-tetramethylxylene diisocyanate (m-TMXDI); para-tetramethylxylene diisocyanate (p-TMXDI); trimerized isocyanurate of any polysocyanate, such as isocyanurate of toluene diisocyanate, trimer of diphenylmethane diisocyanate, trimer of tetramethylxylene diisocyanate, isocyanurate of hexamethylene diisocyanate, and mixtures thereof, dimerized uretdione of any polysocyanate, such as uretdione of toluene diisocyanate, uretdione of hexamethylene diisocyanate, and mixtures thereof; modified polysocyanate derived from the above isocyanates and polyisocyanates; and mixtures thereof.

In view of the advantages of injection molding versus the more complex casting process, under some circumstances it is advantageous to have formulations which are able to cure as a thermoset but only within a specified temperature range which is above that of the typical injection molding process. This allows parts, such as golf ball cover layers, to be initially injection molded, followed by subsequent processing at higher temperatures and pressures to induce further crosslinking and curing, resulting in thermoset properties in the final part. Such an initially injection moldable composition thus called a post curable urethane or urea composition.

If a post curable reduced-yellowing urethane composition is required, a modified or blocked diisocyanate which subsequently unblocks and induces further crosslinking post extrusion may be included in the diisocyanate starting material. Modified isocyanates used for making the polyurethanes generally are defined as chemical compounds containing isocyanate groups that are not reactive at room temperature, but that become reactive once they reach a characteristic temperature. The resulting isocyanates can act as crosslinking agents or chain extenders to form crosslinked polyurethanes. The degree of crosslinking is governed by type and concentration of modified isocyanate presented in the composition. The modified isocyanate used in the composition preferably is selected, in part, to have a characteristic temperature sufficiently high such that the urethane in the composition will retain its thermoplastic behavior during initial processing (such as injection molding). Too low of a characteristic temperature will result in crosslinking of the composition before processing is completed, leading to processing difficulties. The modified isocyanate preferably is selected from the group consisting of: isophorone diisocyanate (IPDI)-based uredione-type crosslinker, a combination of a uredione adduct of IPDI and a partially e-caprolactam-modified IPDI; a combination of isocyanate adducts modified by e-caprolactam and a carboxylic acid functional group; a caprolactam-modified Desmodur diisocyanate; a Desmodur diisocyanate having a 3,5-dimethyl pyrazole modified isocyanate; or mixtures of these. Particular preferred examples of modified isocyanates include those marketed under the trade name CRELAN by Bayer Corporation. Examples of these include: CRELAN TP LS 2147; CRELAN NI 2; isophorone diisocyanate (IPDI)-based uredione-type crosslinker, such as CRELAN VP LS 2347; a combination of a uredione adduct of IPDI and a partially e-caprolactam-modified IPDI, such as CRELAN VP LS 2386; a combination of isocyanate adducts modified by e-caprolactam and a carboxylic acid functional group, such as CRELAN VP LS 2181/1; a caprolactam-modified Desmodur diisocyanate, such as CRELAN NWS; and a Desmodur diisocyanate having a 3,5-dimethyl pyrazole modified isocyanate, such as CRELAN XP 7180. These modified isocyanates may be used either alone or in combination. Such modified isocyanates are described in more detail in U.S. Pat. No. 6,939,924, the entire contents of which are hereby incorporated by reference.

As an alternative if a post curable polyurethane or polyurea composition is required, the diisocyanate may further comprise reaction product of a nitroso compound and a diisocyanate or a polysocyanate. The reaction product has a characteristic temperature at which it decomposes regenerating the nitroso compound and diisocyanate or polysocyanate, which can, by judicial choice of the post processing temperature, in turn induce further crosslinking in the originally thermoplastic composition resulting in thermoset-like properties. Such nitroso compounds are described in more detail in U.S. Pat. No. 7,037,985 B2, the entire contents of which are hereby incorporated by reference.

Any polyol available to one of ordinary skill in the polyurethane art is suitable for use according to the invention. Polyols suitable for use in the reduced-yellowing compositions of the present invention include, but are not limited to, polyester polyols, polyether polyols, polycarbonate polyols and polydiene polyols such as polybutadiene polyols.

Polyester polyols are prepared by condensation or step-growth polymerization utilizing diacids. Primary diacids for polyester polyols are adipic acid and isomeric phthalic acids. Adipic acid is used for materials requiring added flexibility, whereas phthalic anhydride is used for those requiring rigidity. Some examples of polyester polyols include poly (ethylene adipate) (PEA), poly(diethylene adipate) (PDA), poly(propylene adipate) (PPA), poly(tetramethylene adipate) (PTA), poly(hexamethylene adipate) (PHCA), poly(neopentylene adipate) (PNA), polyols composed of 3-methyl-1,5-pentanediol and adipic acid, random copolymer of PEA and PDA, random copolymer of PEA and PPA, random copolymer of PHT and PNA, caprolactone polyol obtained by the ring-opening polymerization of ε-caprolactone, and polyol obtained by opening the ring of β-methyl-δ-valerolactone with ethylene glycol can be used either alone or in a combination thereof. Additionally, polyester polyl may be composed of a copolymer of at least one of the following acids and at least one of the following:
glycols. The acids include terephthalic acid, isophthalic acid, phthalic anhydride, oxalic acid, malonic acid, succinic acid, pentanedioic acid, hexanedioic acid, octanedioic acid, nonanedioic acid, adipic acid, azelaic acid, sebacic acid, dodecanedioic acid, dimer acid (a mixture), p-hydroxybenzoate, trimellitic anhydride, ɛ-caprolactone, and β-methyl-β-valerolactone. The glycols includes ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentylene glycol, polyethylene glycol, polytetramethylene glycol, 1,4-cyclohexane dimethanol, pentaerythritol, and 3-methyl-1,5-pentanediol.

[0060] Polyether polyols are prepared by the ring-opening addition polymerization of an allyl oxide (e.g. ethylene oxide and propylene oxide) with an initiator of a polyhydric alcohol (e.g. diethylene glycol), which is an active hydride. Specifically, polypropylene glycol (PPG), polyethylene glycol (PEG) or propylene oxide-ethylene oxide copolymer can be obtained. Polytetramethylene ether glycol (PTMG) is prepared by the ring-opening polymerization of tetrahydrofuran, produced by dehydration of 1,4-butanediol or hydrogenation of furan. Tetrahydrofuran can form a copolymer with allyl oxide. Specifically, tetrahydrofuran-propylene oxide copolymer or tetrahydrofuran-ethylene oxide copolymer can be formed. The polyether polyol may be used either alone or in a combination.

[0061] Polycarbonate polyol is obtained by the condensation of a known polyol (polyhydric alcohol) with phosgene, chloroformic acid ester, dialkyl carbonate or dialyl carbonate. Particularly preferred polycarbonate polyol contains a polyol component using 1,6-hexanediol, 1,4-butanediol, 1,3-butanediol, neopentylglycol or 1,5-pentanediol. Polycarbonate polyols can be used either alone or in a combination with other polyols.

[0062] Polydiene polyol includes liquid diene polymer containing hydroxyl groups having an average of at least 1.7 functional groups, and may be composed of diene polymer or diene copolymer having 4 to 12 carbon atoms, or a copolymer of such diene with addition to polymerizable α-olefin monomer having 2 to 2.2 carbon atoms. Specific examples include butadiene homopolymer, isoprene homopolymer, butadiene-styrene copolymer, butadiene-isoprene copolymer, butadiene-acrylonitrile copolymer, butadiene-2-ethyl hexyl acrylate copolymer, and butadiene-n-octadeyl acrylate copolymer. These liquid diene polymers can be obtained, for example, by heating a conjugated diene monomer in the presence of hydrogen peroxide in a liquid reactant.

[0063] Polylutadiene polyol includes liquid diene polymer containing hydroxyl groups having an average of at least 1.7 functional groups, and may be composed of diene polymer or diene copolymer having 4 to 12 carbon atoms, or a copolymer of such diene with addition to polymerizable α-olefin monomer having 2 to 2.2 carbon atoms. Specific examples include butadiene homopolymer, isoprene homopolymer, butadiene-styrene copolymer, butadiene-isoprene copolymer, butadiene-acrylonitrile copolymer, butadiene-2-ethyl hexyl acrylate copolymer, and butadiene-n-octadeyl acrylate copolymer. These liquid diene polymers can be obtained, for example, by heating a conjugated diene monomer in the presence of hydrogen peroxide in a liquid reactant.

[0064] Any polyamine available to one of ordinary skill in the polyurethane art is suitable for use according to the invention. Polymers suitable for use in the reduced-yellowing compositions of the present invention include, but are not limited to, amine-terminated hydrocarbons, amine-terminated polyethers, amine-terminated polyesters, amine-terminated polycapro lactones, amine-terminated polycarbonates, amine-terminated polyamides, and mixtures thereof. The amine-terminated compound may be a polyether amine selected from polytetramethylene ether diamines, polyoxpropylene diamines, poly(ethylene oxide capped oxypropylene) ether diamines, triethylene glycol diamines, propylene oxide-based triamines, trimethylolpropane-based triamines, glycerin-based triamines, and mixtures thereof.

[0065] The previously described disiocyanate and polyol or polya mine components may be previously combined to form a prepolymer prior to reaction with the chain extender or curing agent. Any such prepolymer combination is suitable for use in the present invention.Commercially available polyisocyanates include LHF580, LHF1120, LHF1170, LHF11570, LF590A, LF590A, LF590A, LF601D, LF751D, LFG963A, LFG640D.

[0066] One preferred prepolymer is a toluene diisocyanate prepolymer with propylene glycol. Such polypropylene glycol terminated toluene diisocyanate prepolymer are available from Uniroyal Chemical Company of Middlebury, Conn., under the trade name ADIPRENE® LF9663A and LF964OD. Most preferred prepolymer are the polytetramethylene ether glycol terminated toluene diisocyanate prepolymer including those available from Uniroyal Chemical Company of Middlebury, Conn., under the trade name ADIPRENE® LF930A, LF950A, LF601D, and LF751D.

[0067] In one embodiment, the number of free NCO groups in the urethane or urea prepolymer may be less than about 14 percent. Preferably the urethane or urea prepolymer has from about 3 percent to about 11 percent, more preferably from about 4 to about 9.5 percent and even more preferably from about 3 percent to about 9 percent free NCO on an equivalent weight basis.

[0068] Polyl chain extenders or curing agents may be primary, secondary, or tertiary polyols. Non-limiting examples of monomers of these polyols include: trimethylol propane (TMP), ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, propylene glycol, dipropylene glycol, 1,2-butanediol, 1,3-butanediol, 2,3-butanediol, 1,2-pentanediol, 2,3-pentanediol, 2,5-hexanediol, 2,4-hexanediol, 2-ethyl-1,3-hexanediol, cyclohexanediol, and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol. Diamines also can be added to urethane prepolymer to function as chain extenders.

[0069] Diamines and other suitable polyamines may be added to the compositions to function as chain extenders or curing agents. These include primary, secondary and tertiary amines having two or more amines as functional groups. Examples of these include: aliphatic diamines, such as tetramethylenediamine, pentamethylenediamine, hexamethylenediamine; alicyclic diamines, such as 3,3'-dimethyl-4,4'-diamino-dicyclohexyl methane; and aromatic diamines, such as diethyl-2,4-toluenediamine, 4,4'-methylenebis-(3-chloro, 2,6-diethyl)-aniline (available from Air Products and Chemicals Inc., of Allentown, Pa., under the trade name LONZA-CURE®), 3,3'-dichlorobenzidene, 3,3'-dichloro-4,4'-diaminodiphenyl methane (MOCA): N,N,N',N'-tetraakis(2-hydroxypropyloxy)ethylendiamine, 3,5-dimethylthio-2,4-toluenediamine; 3,5-dimethylothio-2,6-toluenediamine; N,N'-diallyl diaminodiphenyl methane; trimethyleneglycol-di-p-aminobenzoate; 3,5-di, 3,5'-polyltetramethyleneoxide-di-p-aminobenzoate, 4,4'-methylenebis-2-chloroanilines, 2,2',3,3'-
Further examples include ethylene diamine; 1-methyl-2,6-cyclohexyl diamine; 2,2,4- and 2,4,4-trimethyl-1,6-hexanedi amine; 4,4'-bis-(sec-butylamino)-dicyclohexyl methane; 1,4-bis-(sec-butylamino)-cyclohexane; 1,2-bis-(sec-butylamino)-cyclohexane; derivatives of 4,4'-bis-(sec-butylamino)-dicyclohexymethane; 4,4'-dicyclohexylmethane diamine; 1,4-cyclohexane-bis(methylene); 1,3-cyclohexane-bis(methylene); diethylene glycol bis-(aminopropyl) ether; 2-methylpentamethylene diamine; dianisocyclohexane; diethylene triamine; triethylene tetramine; tetramethylene pentamine; propylene diamine; 1,3-dimethylaminopropylamine; diethylamine propylene diamine; imido-bis-propyleneamine; monoethanolamine; diethanolamine; triethanolamine; monoiso propylamine, diisopropylamine; isophoronediamine; and mixtures thereof.

Aromatic diamines have a tendency to provide a stiffener (i.e., having a higher Mooney viscosity) product than aliphatic or cycloaliphatic diamines.

Depending on their chemical structure, curing agents may be slow- or fast-reacting polyamines or polyols as described in U.S. Pat. Nos. 6,793,864, 6,719,646 and copending US Patent Publication No. 2004/0201133 A1, (the contents of all of which are hereby incorporated herein by reference). Slow-reacting polyamines are diamines that have amine groups which are sterically and/or electronically hindered by electron withdrawing groups or bulky groups situated proximate to the amine reaction sites. The spacing of the amine reaction sites will also affect the reactivity speed of the polyamines. Suitable curatives are selected from the slow-reacting polyamine group include, but are not limited to, 3,5-dimethylthio-2,4-toluenedi amine; 3,5-dimethylthio-2,6-toluenediamine; N,N'-dialkylamidodiphenyl methane; trimethylene glycol-di-p-amino benzoate; polytetramethyleneoxide-di-p-amino benzoate, and mixtures thereof. Of these, 3,5-dimethylthio-2,4-toluenediamine and 3,5-dimethylthio-2,6-toluenediamine are isomers and are sold under the trade name ETHACURE® 300 by Ethyl Corporation. Trimethylene glycol-di-p-amino benzoate is sold under the trade name POLACURE® 740M and polytetramethyleneoxide-di-p-amino benzoates are sold under the trade name POLAMINES® by Polaron Corporation. N,N'-dialkylamidodiphenyl methane is sold under the trade name UNILINK® by UOP.

When slow-reacting polyamines are used as the curing agent to produce urethane elastomers, a catalyst is typically needed to promote the reaction between the urethane prepolymer and the curing agent. Suitable catalysts include TEDA dissolved in di propylene glycol (such as TEDA L33 available from Wito Corp. Greenwich, Conn., and DABCO 33 LV available from Air Products and Chemicals Inc.), which may be added in amounts of 2-5%, and more preferably TEDA dissolved in 1,4-butane diol which may be added in amounts of 2-5%. Another suitable catalyst includes a blend of 0.5% 33LV or TEDA L33 (above) with 0.1% dibutyl tin dilaurate (available from Wito Corp. or Air Products and Chemicals, Inc.) which is added to a curative such as VIBRACURE® A250. Unfortunately, as is well known in the art, the use of a catalyst can have a significant effect on the ability to control the reaction and thus, on the overall processability.

To eliminate the need for a catalyst, a fast-reacting curing agent can be used which do not have electron withdrawing groups or bulky groups that interfere with the reaction groups. However, the problem with lack of control associated with the use of catalysts is not completely eliminated since fast-reacting curing agents are also relatively difficult to control.

In one embodiment the dicyanamidine may be used in a blend with either a slower or faster curing agent to eliminate the problems associated with using either type of curing agent in isolation. The ultimate result of such a combination is the realization of greater control and concomitant flexibility over the reactions used to produce the polyurethanes or polyureas. Preferably the dicyanamidine is used in combination with a faster curing agent.

Preferred curing agent blends include the use of fast curing agents such as diethyl-2,4-toluenedia mine, 4,4'-methylenediphenyl-3-chloro,2,6-diethyl-aniline (available from Air Products and Chemicals Inc., of Allentown, Pa., under the trade name LONZACURE®, 3,3'-dichlorobenzidine; 3,3'-dichloro-4,4'-diaminodiphenyl methane (MOCA); N,N',N'-tetraakis(2-hydroxypropyl)ethylendiamine and Curalon L, a trade name for a mixture of aromatic diamines sold by Uniproyal, Inc. or any and all combinations thereof. A preferred fast-reacting curing agent is diethyl-2,4-toluenediamine, which has two commercial grades names, Ethacure® 100 and Ethacure® 100LC commercial grade has lower color and less by-product. In other words, it is considered a cleaner product to those skilled in the art.

Advantageously, the use of the Ethacure® 100LC commercial grade results in a golf ball that is less susceptible to yellowing when exposed to UV light conditions. A player appreciates this desirable aesthetic effect although it should be noted that either of these two commercial grades may be used for the curing agent diethyl-2,4-toluenedia mine.

If a post curable composition is required it is the chain extender or curing agent can further comprise a peroxide or peroxide mixture. Before the composition is exposed to sufficient thermal energy to reach the activation temperature of the peroxide, the composition of (a) and (b) behaves as a thermoplastic material. Therefore, it can readily be formed into golf ball layers using injection molding. However, when sufficient thermal energy is applied to bring the composition above the peroxide activation temperature, crosslinking occurs, and the thermoplastic polyurethane is converted into crosslinked polyurethane.

Examples of suitable peroxides for use in compositions within the scope of the present invention include aliphatic peroxides, aromatic peroxides, cycled peroxides, or mixtures of these. Primary, secondary, or tertiary peroxides can be used, with tertiary peroxides most preferred. Also, peroxides containing more than one peroxo group can be used, such as 2,5-bis-(tert-butylperoxy)-2,5-dimethyl hexane and 1,4-bis-(tert-butylperoxy-isopropyl)-benzene. Also, peroxides that are either symmetrical or asymmetric can be used, such as tert-butylperbenzoate and tert-butylcumyl peroxide. Additionally, peroxides having carboxy groups also can be used. Decomposition of peroxides can be brought about by applying thermal energy, shear, reactions with other chemical ingredients, or a combination of these. Homolytically decomposed peroxide, heterolytically decomposed peroxide, or a mixture of these can be used to promote crosslinking reactions in compositions. Examples of suitable aliphatic peroxides and aromatic peroxides, include diacetoxyperoxide, di-
tert-butylperoxide, dibenzoylperoxide, dicumylperoxide, 2,5-bis-(t-butylperoxy)-2,5-dimethyl hexane, 2,5-dimethyl-2,5-di(benzyloperoxy)hexane, 2,5-dimethyl-2,5-di(butylperoxy)-3-hexyne, n-butyl-4,4-bis(t-butylperoxy) valerate, 1,4-bis-(t-butylperoxyisopropyl)-benzene, t-butyloxybenzoate, 1,1-bis-(t-butyloxy)-3,3,5 tri-methylcyclohexane, and di(2,4-dichloro-benzyl). Peroxides may be acquired from Akzo Nobel Polymer Chemicals of Chicago, Ill., Atofina of Philadelphia, Pa. and Akrochem of Akron, Ohio. Further details of this post cure system are disclosed in U.S. Pat. No. 6,924,337, the entire contents of which are hereby incorporated by reference.

Polymeric materials generally considered useful for making golf balls may also be included in the components of the golf balls and these include, without limitation, synthetic and natural rubbers, thermoset polymers such as other thermostet polyurethanes or thermoset polyureas, as well as thermoplastic polymers including thermoplastic elastomers such as metalloocene catalyzed polymer, unimodal ethylene/carboxylic acid copolymers, unimodal ethylene/carbonic acid/carboxylic acid terpolymers, bimodal ethylene/carboxylic acid copolymers, bimodal ethylene/carbonic acid/epoxy terpolymers, unimodal ionomers, bimodal ionomers, modified unimodal ionomers, modified bimodal ionomers, thermoplastic polyurethanes, thermoplastic polyurea, polyanides, polycaprolactams, polysters, copolysters, copolycarbonates, polylefins, halogenated (e.g. chlorinated) polylefins, halogenated polyalkylene compounds, such as halogenated polyethylene [e.g. chlorinated polyethylene (CPE)], polyalkylmer, polyphenylene oxides, polyphenylene sulfides, diallyl phthalate polymers, polymides, polyvinyl chlorides, polyamide-ionomers, polyurethane-ionomers, polyvinyl alcohols, polyarylates, polyacrylates, polyphenylene ethers, impact-modified polyphenylene ethers, polystyrenes, high impact polystyrenes, acrylonitrile-butadiene-styrene copolymers, styrene-acrylonitrile (SAN), acrylonitrile-styrene-acrylonitrile, styrene-maleic anhydride (S/MA) polymers, styrene copolymers, functionalized styrenic copolymers, functionalized styrenic terpolymers, styrenic terpolymers, cellulosic polymers, liquid crystal polymers (LCP), ethylene-propylene-diene terpolymers (EPDM), ethylene-vinyl acetate copolymers (EVA), ethylene-propylene copolymers, ethylene vinyl acetates, polyureas, and polysiloxanes and any and all combinations thereof.

Examples of copolyester thermoplastic elastomers include polyether ester block copolymers, polyolactone ester block copolymers, and aliphatic and aromatic dicarboxylic acid copolymerized polyesters. Polyether ester block copolymers are copolymers comprising polyester hard segments polymerized from a dicarboxylic acid and a low molecular weight diol, and polyester soft segments polymerized from an alkylene glycol having 2 to 10 atoms. Polyolactone ester block copolymers are copolymers having polyolactone chains instead of polyester as the soft segments discussed above for polyether ester block copolymers. Aliphatic and aromatic dicarboxylic acid copolymerized polyesters are copolymers of an acid component selected from aromatic dicarboxylic acids, such as terephthalic acid and isophthalic acid, and aliphatic acids having 2 to 10 carbon atoms with at least one diol component, selected from aliphatic and alicyclic diols having 2 to 10 carbon atoms. Blends of aromatic polyester and aliphatic polyester also may be used for these. Examples of these include products marketed under the trade names HYTREL by E.I. duPont de Nemours & Company, and SKYPEL by S.K. Chemicals of Seoul, South Korea.

Examples of other thermoplastic elastomers include multiblock, rubber-based copolymers, particularly those in which the rubber block component is based on butadiene, isoprene, or ethylene/butylene. The non-rubber repeating units of the copolymer may be derived from any suitable monomer, including met(acrylate) esters, such as methyl methacrylate and cyclohexylmethacrylate, and vinyl arylene, such as styrene. Styrene block copolymers are copolymers of styrene with butadiene, isoprene, or a mixture of the two. Additional unsaturated monomers may be added to the structure of the styrenic block copolymer as needed for property modification of the resulting SBC/urethane copolymer. The styrenic block copolymer can be a diblock, a triblock styrenic polymer. Examples of such styrenic block copolymers are described in, for example, U.S. Pat. No. 5,436,295 to Nishikawa et al., which is incorporated herein by reference. The styrenic block copolymer can have any known molecular weight for such polymers, and it can possess a linear, branched, star, dendrimeric or combination molecular structure. The styrenic block copolymer can be unmodified by functional groups, or it can be modified by hydroxyl group, carboxyl group, or other functional groups, either in its chain structure or at one or more terminus. The styrenic block copolymer can be obtained using any common process for manufacture of such polymers. The styrenic block copolymer also may be hydrogenated using well-known methods to obtain a partially or fully saturated diene monomer block. Examples of styrenic copolymers include, without limitation, resins manufactured by Kraton Polymers (formerly of Shell Chemicals) under the trade names KRATON D (for styrene-butadiene-styrene and styrene-isoprene-styrene types), and KRATON G (for styrene-ethylene-butylene-styrene and styrene-ethylene-propylene-styrene types) and Kuraray under the trade name SEPTON. Examples of randomly distributed styrenic polymers include paramethylstyrene-isobutylene (isotprene) copolymers developed by ExxonMobil Chemical Corporation and styrene-butadiene random copolymers developed by Chevron Phillips Chemical Corporation.

Examples of other thermoplastic elastomers suitable as additional polymer components include those having functional groups, such as carboxylic acid, maleic anhydride, glycidyl, norbornene, and hydroxyl functionalities. An example of these includes a block polymer having at least one polymer block A comprising an aromatic vinyl compound and at least one polymer block B comprising a conjugated diene compound, and having a hydroxyl group at the terminal block copolymer, or its hydrogenated product. An example of this polymer is sold under the trade name SEPTON HG-252 by Kuraray Company of Kurashiki, Japan. Other examples of these include: maleic anhydride functionalized triblock copolymer consisting of polystyrene end blocks and poly (ethylene-butylene), sold under the trade name KRATON FG 1901X by Shell Chemical Company; maleic anhydride modified ethylene-vinyl acetate copolymer, sold under the trade name FUSABOND by E.I. du Pont de Nemours & Company; ethylene-isobutyl acrylate-methacrylic acid terpolymer, sold under the trade name NUCREL by E.I. du Pont de Nemours & Company; ethylene-ethyl acrylate-methacrylaldehyde terpolymer, sold under the trade name BONDINE AX 8390 and 8660 by Sumitomo Chemical Industries; brominated styrene-isobutylene copolymers sold under the trade name BROMO XP-50 by Exxon Mobility Corporation; and resins
having glycidyl or maleic anhydride functional groups sold under the trade name LOTADER by Elf Atochem of Puteaux, France.

[0084] The outer cover and/or one or more intermediate layers of the golf ball may comprise one or more ionomer resins. One family of such resins was developed in the mid-1960's, by E.I. DuPont de Nemours and Co., and sold under the trademark SURLYN®. Preparation of such ionomers is well known, for example see U.S. Pat. No. 3,264,272. Generally speaking, most commercial ionomers are unimodal and consist of a polymer of a mono-olefin, e.g., an-alkene, with an unsaturated mono- or dicarboxylic acids having 3 to 12 carbon atoms. An additional monomer in the form of a mono- or dicarboxylic acid ester may also be incorporated in the formulation as a so-called “softening comonomer”. The incorporated carboxylic acid groups are then neutralized by a basic metal ion salt, to form the ionomer. The metal cations of the basic metal ion salt used for neutralization include Li⁺, Na⁺, K⁺, Zn⁺², Ca⁺², Co⁺², Ni⁺², Cu⁺², Pb⁺², and Mg⁺², with the Li⁺, Na⁺, Ca⁺², Zn⁺², and Mg⁺² being preferred. The basic metal ion salts include those of for example formic acid, acetic acid, nitric acid, and carbonic acid, hydrogen carbonate salts, oxides, hydroxides, and alkoxides.

[0085] The first commercially available ionomer resins contained up to 16 weight percent acrylic or methacrylic acid, although it was also well known at that time that, as a general rule, the hardness of these cover materials could be increased with increasing acid content. Hence, in Research Disclosure 29703, published in January 1989, DuPont disclosed ionomers based on ethylene/acrylic acid or ethylene/methacrylic acid containing acid contents of greater than 15 weight percent. In this same disclosure, DuPont also taught that such so-called “high acid ionomers” had significantly improved stiffness and hardness and thus could be advantageously used in golf ball construction, when used either singly or in a blend with other ionomers.

[0086] More recently, high acid ionomers can be ionomer resins with acrylic or methacrylic acid units present from 16 wt.% to about 35 wt.% in the polymer. Generally, such a high acid ionomer will have a flexural modulus from about 50,000 psi to about 125,000 psi.

[0087] Ionomer resins further comprising a softening comonomer, present from about 10 wt.% to about 50 wt.% in the polymer, have a flexural modulus from about 2,000 psi to about 10,000 psi, and are sometimes referred to as “soft” or “very low modulus” ionomers. Typical softening comonomers include n-butyl acrylate, iso-butyl acrylate, n-butyl methacrylate, methyl acrylate and methyl methacrylate.

[0088] Today, there are a wide variety of commercially available ionomer resins based both on copolymers of ethylene and (meth)acrylic acid or terpolymers of ethylene and (meth)acrylic acid and (meth)acrylate, all of which contain of which are be used as a golf ball component. The properties of these ionomer resins can vary widely due to variations in acid content, softening comonomer content, the degree of neutralization, and the type of metal ion used in the neutralization. The full range commercially available typically includes ionomers of polymers of general formula, E/X/Y polymer, wherein E is ethylene, X is a C₃ to C₅ α,β ethylenically unsaturated carboxylic acid, such as acrylic or methacrylic acid, and is present in an amount from about 2 to about 30 weight % of the E/X/Y copolymer, and Y is a softening comonomer selected from the group consisting of alkyl acrylate and alkyl methacrylate, such as methyl acrylate or methyl methacrylate, and wherein the alkyl groups have from 1-8 carbon atoms, Y is in the range of 0 to about 50 weight % of the E/X/Y copolymer, and wherein the acid groups present in said ionomeric polymer are partially neutralized with a metal selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc or aluminum, and combinations thereof.

[0089] E/X/Y, where E is ethylene, X is a softening comonomer such as present in an amount of from 0 wt.% to about 50 wt. % of the polymer, and Y is present in an amount from about 5 wt. % to about 35 wt. % of the polymer, and wherein the acid moiety is neutralized from about 1% to about 100% to form an ionomer with a cation such as lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc or aluminum, or a combination of such cations.

[0090] The ionomer may also be a so-called bimodal ionomer as described in U.S. Pat. No. 6,562,906 (the entire contents of which are herein incorporated by reference). These ionomers are bimodal as they are prepared from blends comprising polymers of different molecular weights. Specifically they include bimodal polymer blend compositions comprising:

[0091] a) a high molecular weight component having molecular weight of about 80,000 to about 500,000 and comprising one or more ethylene/α, β-ethylenically unsaturated C₃-₅ carboxylic acid copolymers and/or one or more ethylene, alkyl (meth)acrylate, (meth)acrylic acid terpolymers; said high molecular weight component being partially neutralized with metal ions selected from the group consisting of lithium, sodium, zinc, calcium, magnesium, and a mixture of any these; and

[0092] b) a low molecular weight component having a molecular weight of about from about 2,000 to about 30,000 and comprising one or more ethylene/α, β-ethylenically unsaturated C₃-₅ carboxylic acid copolymers and/or one or more ethylene, alkyl (meth)acrylate, (meth)acrylic acid terpolymers; said low molecular weight component being partially neutralized with metal ions selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc or aluminum, and a mixture of any of these.

[0093] In addition to the unimodal and bimodal ionomers, also included are the so-called “modified ionomers” examples of which are described in U.S. Pat. Nos. 6,100,321, 6,329,458 and 6,616,552 and U.S. Patent Publication US 2003/0158312 A1, the entire contents of all of which are herein incorporated by reference.

[0094] The modified unimodal ionomers may be prepared by mixing:

[0095] a) an ionomeric polymer comprising ethylene, from 5 to 25 weight percent (meth)acrylic acid, and from 0 to 40 weight percent of a (meth)acrylate monomer, said ionomeric polymer neutralized with metal ions selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc or aluminum, and any and all mixtures thereof; and

[0096] b) from about 5 to about 40 weight percent (based on the total weight of said modified ionomeric polymer) of one or more fatty acids or metal salts of said fatty acid, the metal selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc or aluminum, and any and all mixtures thereof; and the fatty acid preferably being stearic acid.
[0097] The modified bimodal ionomers, which are ionomers derived from the earlier described bimodal ethylene/carboxylic acid copolymers (as described in U.S. Pat. No. 6,562,906, the entire contents of which are herein incorporated by reference), are prepared by mixing:

[0098] a) a high molecular weight component having a molecular weight of about 80,000 to about 500,000 and comprising one or more ethylene units, β-ethylenically unsaturated C₃₋₈ carboxylic acid copolymers and/or one or more ethylene, alkyl (meth)acrylate, (meth)acrylic acid terpolymers; said high molecular weight component being partially neutralized with metal ions selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc or aluminum, and any and all mixtures thereof; and

[0099] b) a low molecular weight component having a molecular weight of about from about 2,000 to about 30,000 and comprising one or more ethylene units, β-ethylenically unsaturated C₃₋₈ carboxylic acid copolymers and/or one or more ethylene, alkyl (meth)acrylate, (meth)acrylic acid terpolymers; said low molecular weight component being partially neutralized with metal ions selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc or aluminum, and any and all mixtures thereof; and

[0100] c) from about 5 to about 40 weight percent (based on the total weight of said modified ionomeric polymer) of one or more fatty acids or metal salts of said fatty acid, the metal selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc or aluminum, and any and all mixtures thereof; and the fatty acid preferably being stearic acid.

[0101] The fatty or waxy acid salts utilized in the various modified ionomers are composed of a chain of alkyl groups containing from about 4 to 75 carbon atoms (usually even numbered) and characterized by a −COOH terminal group. The generic formula for all fatty and waxy acids above acetic acid is CH₃(CH₂)ₓCOOH, where the carbon atom count includes the carboxyl group (i.e., x=2-73). The fatty or waxy acids utilized to produce the fatty or waxy acid salts modifiers may be saturated or unsaturated, and they may be present in solid, semi-solid or liquid form.

[0102] Examples of suitable saturated fatty acids, i.e., fatty acids in which the carbon atoms of the alkyl chain are connected by single bonds, include but are not limited to stearic acid (C₁₈₋₂₀, i.e., CH₃(CHOH)₁₇COOH), palmitic acid (C₁₆₋₁₇, i.e., CH₃(CHOH)₁₄COOH), palgolic acid (C₁₈₋₁₉, i.e., CH₃(CHOH)₁₃COOH) and lauric acid (C₁₂₋₁₃, i.e., CH₃(CHOH)₁₀OCOOH). Examples of suitable unsaturated fatty acids, i.e., fatty acids in which there are one or more double bonds between the carbon atoms in the alkyl chain, include but are not limited to oleic acid (C₁₇₋₁₈, i.e., CH₃(CHOH)₇CH=CH(CH₂)₆COOH).

[0103] The source of the metal ions used to produce the metal salts of the fatty or waxy acid salts used in the various modified ionomers are generally various metal salts which provide the metal ions capable of neutralizing, to various extents, the carboxylic acid groups of the fatty acids. These include the sulfate, carbonate, acetate and hydroxylate salts of zinc, barium, calcium and magnesium.

[0104] Since the fatty acid salts modifiers comprise various combinations of fatty acids neutralized with a large number of different metal ions, several different types of fatty acid salts may be utilized, including metal stearates, laureates, oleates, and palmitates, with calcium, zinc, sodium, lithium, potassium and magnesium stearate being preferred, and calcium and sodium stearate being most preferred.

[0105] The fatty or waxy acid or metal salt of said fatty or waxy acid is present in the modified ionomeric polymers in an amount of from about 5 to about 40, preferably from about 7 to about 35, more preferably from about 8 to about 20 weight percent (based on the total weight of said modified ionomeric polymer).

[0106] As a result of the addition of the one or more metal salts of a fatty or waxy acid, from about 40 to 100, preferably from about 50 to 100, more preferably from about 70 to 100 percent of the acidic groups in the final modified ionomeric polymer composition are neutralized by a metal ion.

[0107] An example of such a modified ionomeric polymer is DuPont® HPF-1000 available from E.I. DuPont de Nemours and Co. Inc.

[0108] A preferred ionomer composition may be prepared by blending one or more of the unimidom ionomers, bimodal ionomers, or modified unimidom or bimodal ionomeric polymers as described herein, and further blended with a zinc neutralized ionomer of a polymer of general formula EₓYₓ where E is ethylene, X is a softening comonomer such as acrylate or methacrylate and in present in an amount of from 0 to about 50, preferably 0 to about 25, most preferably 0, and Y is acrylic or methacrylic acid and is present in an amount from about 5 wt. % to about 25, preferably from about 10 to about 25, and most preferably about 10 to about 20 wt % of the total composition.

[0109] A “specialty propylene elastomer” includes a thermoplastic propylene-ethylene copolymer composed of a majority amount of propylene and a minority amount of ethylene. These copolymers have at least partial crystallinity due to adjacent isotactic propylene units. Although not bound by any theory, it is believed that the crystalline segments are physical crosslinking sites at room temperature, and at high temperature (i.e., about the melting point), the physical crosslinking is removed and the copolymer is easy to process. According to one embodiment, a specialty propylene elastomer includes at least about 50 mole % propylene co-monomer. Specialty propylene elastomers can also include functional groups such as maleic anhydride, glycidyl, hydroxyl, and/or carboxylic acid. Suitable specialty propylene elastomers include propylene-ethylene copolymers produced in the presence of a metalloocene catalyst. More specific examples of specialty propylene elastomers are illustrated below.

[0110] One example of illustrative specialty propylene elastomers is described in U.S. Pat. No. 6,525,157, to Kim et al., the entire contents of which is hereby incorporated by reference in its entirety. Specialty propylene elastomers are commercially available under the tradename VISTAMAXX from ExxonMobil Chemical.

[0111] In yet another embodiment, a blend of an ionomer and a block copolymer can be included in the composition that includes the specialty propylene elastomer. An example of a block copolymer is a functionalized styrene block copolymer, the block copolymer incorporating a first polymer block having an aromatic vinyl compound, a second polymer block having a conjugated diene compound, and a hydroxyl group located at a block copolymer, or its hydrogenation product, in which the ratio of block copolymer to ionomer ranges from 5:95 to 95:5 by weight, more preferably from about 10:90 to about 90:10 by weight, more preferably from
about 20:80 to about 80:20 by weight, more preferably from about 30:70 to about 70:30 by weight and most preferably from about 35:65 to about 65:35 by weight. A preferred block copolymer is SEPTON HG-252. Such blends are described in more detail in commonly-assigned U.S. Pat. No. 6,861,474 and U.S. Patent Publication No. 2003/0224871 both of which are incorporated herein by reference in their entireties.

In a further embodiment, the core, mantle and/or cover layers can comprise a composition prepared by blending together at least three materials, identified as Components A, B, and C, and melt-processing these components to form in-situ, a polymer blend composition incorporating a pseudo-crosslinked polymer network. Such blends are described in more detail in commonly-assigned U.S. Pat. No. 6,930,150, to Kim et al., the content of which is incorporated by reference herein in its entirety. Component A is a monomer, oligomer, prepolymers or polymer that incorporates at least five percent by weight of at least one type of an acidic functional group. Examples of such polymers suitable for use as include, but are not limited to, ethylene/(meth)acrylic acid copolymers and ethylene/(meth)acrylic acid/alkyl(meth)acrylate terpolymers, or ethylene and/or propylene maleic anhydride copolymers and terpolymers. Examples of such polymers which are commercially available include, but are not limited to, the ExxonMobil 5000, 5001, 5020, 5050, 5070, 5100, 5110 and 5200 series of ethylene-acrylic acid copolymers sold by Exxon and the PRIMACOR® 1321, 1410, 1410-X, 1420, 1430, 2912, 3150, 3330, 3340, 3440, 3460, 4311, 4608 and 5080 series of ethylene-acrylic acid copolymers sold by The Dow Chemical Company, Midland, Mich. and the ethylene-acrylic acid copolymers Nucrel 599, 699, 9093, 9010, 925, 960, 2806 and 2906 ethylene-methacrylic acid copolymers sold by DuPont.

Also included are the bimodal ethylene/carboxylic acid copolymers as described in U.S. Pat. No. 6,562,906, the contents of which are incorporated herein by reference. These polymers comprise ethylene/α, β-ethylenically unsaturated Cα-carboxylic acid high copolymers, particularly ethylene(meth)acrylic acid copolymers and ethylene, alkyl(meth) acrylate, (meth)acrylic acid terpolymers, having molecular weights of about 80,000 to about 500,000 which are melt blended with ethylene/α, β-ethylenically unsaturated Cα-Cβ-carboxylic acid copolymers, particularly ethylene/(meth) acrylic acid copolymers having molecular weights of about 2,000 to about 30,000.

As discussed above, Component B can be any monomer, oligomer, or polymer, preferably having a lower weight percentage of anionic functional groups than that present in Component A in the weight ranges discussed above, and most preferably free of such functional groups. Preferred materials for use as Component B include polyester elastomers marketed under the name PEBA or LINDA by ATOFINA Chemicals of Philadelphia, Pa.; HYTREL, FUSABOND, and NUCREL marketed by E.I. DuPont de Nemours & Co. of Wilmington, Del.; SKYPOL and SKYTHANE by S.K. Chemical Co of Seoul, South Korea; SEPTON and HYBRAR marketed by Kuraray Company of Kurashiki, Japan; ESTHANE by Noveon; and KRAFON marketed by Krafcin Polymers. A most preferred material for use as Component B is SEPTON HG-252.

Component C is a base capable of neutralizing the acidic functional group of Component A and is base having a metal cation. These metals are from groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIA, VIIA, VIIB and VIIIB of the periodic table. Examples of these metals include lithium, sodium, magnesium, aluminum, potassium, calcium, manganese, tungsten, titanium, iron, cobalt, nickel, hafnium, copper, zinc, barium, zirconium, and tin. Suitable metal compounds for use as a source of Component C are, for example, metal salts, preferably metal hydroxides, metal oxides, metal carbonates, or metal acetates. In addition to Components A, B, and C, other materials commonly used in polymer blend compositions, can be incorporated into compositions prepared using the method of the present invention, including: crosslinking agents, co-crosslinking agents, accelerators, activators, UV-active chemicals such as UV initiators, EB-active chemicals, colorants, UV stabilizers, optical brighteners, antioxidants, processing aids, mold release agents, foaming agents, and organic, inorganic or metallic fillers or fibers, including fillers to adjust specific gravity.

The composition preferably is prepared by mixing the above materials into each other thoroughly, either by using a dispersive mixing mechanism, a distributive mixing mechanism, or a combination of these. These mixing methods are well known in the manufacture of polymer blends. As a result of this mixing, the anionic functional group of Component A is dispersed evenly throughout the mixture. More preferably, Components A and B are melt-mixed together without Component C, with or without the premixing discussed above, to produce a melt-mixture of the two components. Then, Component C is separately mixed into the blend of Components A and B. This mixture is melt-mixed to produce the reaction product. This two-step mixing can be performed in a single process, such as, for example, an extrusion process using a proper barrel length or screw configuration, along with a multiple feeding system.

Illustrative polymers for use in the compositions/golf balls disclosed include those obtained by: (1) polycondensation of (a) a dicarboxylic acid, such as oxalic acid, adipic acid, sebacic acid, terephthalic acid, isophthalic acid, or 1,4-cyclohexanedicarboxylic acid, with (b) a diamine, such as ethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, decamethylenediamine, 1,4-cyclohexyldiamine or m-xylylenediamine; (2) a ring-opening polymerization of cyclic lactam, such as ε-caprolactam or ω-lauralactam; (3) polycondensation of an aninocarboxylic acid, such as 6-aminocaproic acid, 9-aminoxanonic acid, 11-aminoundecanoic acid or 12-aminododecanoic acid; (4) copolymerization of a cyclic lactam with a dicarboxylic acid and a diimide; or any combination of (1)-(4). In certain examples, the dicarboxylic acid may be aromatic dicarboxylic acid or a cycloaliphatic dicarboxylic acid. In certain examples, the diimide may be an aliphatic diamine or a cycloaliphatic diimide. Specific examples of suitable polyamides include polyamide 6; polyamide 11; polyamide 12; polyamide 4,6; polyamide 6,6; polyamide 6,9; polyamide 6,10; polyamide 6,12; polyamide MXD6; PA12, CX; PA12, IT; PPA; PA6, IT; and PA6/PP.
One class of copolyamide elastomers are polyether amide elastomers. Illustrative examples of polyether amide elastomers are those that result from the copolycondensation of polyamide blocks having reactive chain ends with polyether blocks having reactive chain ends, including:

1. polyamide blocks of diamine chain ends with polyoxyalkylene sequences of dicarboxylic chains;
2. polyamide blocks of dicarboxylic chain ends with polyoxyalkylene sequences of diamine chain ends obtained by cyanocellulose and hydrogenation of polyoxyalkylene alpha-omega dihydroxylated aliphatic sequences known as polyether diols; and
3. polyamide blocks of dicarboxylic chain ends with polyether diols, the products obtained, in this particular case, being polyetheresteramides.

More specifically, the polyamide elastomer can be prepared by polycondensation of the components (i) a diamine and a dicarboxylate, lactams or an amino dicarboxylic acid (PA component), (ii) a polyoxyalkylene glycol such as polyoxyethylene glycol, propoxy propylene glycol (PG component) and (iii) a dicarboxylic acid.

The polyamide blocks of dicarboxylic chain ends come, for example, from the condensation of alpha-omega amino acid or carboxylic dicarboxylic and diamines in the presence of a carboxylic diacid which limits the chain length. The molecular weight of the polyamide sequences is preferably between about 300 and 15,000, and more preferably between about 600 and 5,000. The molecular weight of the polyether sequences is preferably between about 100 and 6,000, and more preferably between about 200 and 3,000.

The amide block polyamides may also comprise randomly distributed units. These polymers may be prepared by the simultaneous reaction of polyether and precursor of polyamide blocks. For example, the polyether diol may react with a diamine or alpha-omega amino acid and a diacid which limits the chain in the presence of water. A polymer is obtained that has primarily polyamide blocks and/or polyamide blocks of very variable length, but also the various reactive groups that have reacted in a random manner and which are distributed statistically along the polymer chain.

Suitable amide block polyamides include those as disclosed in U.S. Pat. Nos. 4,331,786; 4,115,475; 4,195,015; 4,835,441; 4,864,014; 4,230,848 and 4,352,920.

The polyether block may be, for example, a polyethylene glycol (PEG), a polypoly(propylene glycol (PPG), or a polytetramethylene glycol (PTMG), also designated as polytetrahydrofurane (PTHF). The polyether blocks may be along the polymer chain in the form of diols or diamines. However, for reasons of simplification, they are designated PEG blocks, or PPG blocks, or also PTMG blocks.

The polyether block comprises different units such as units which derive from ethylene glycol, propylene glycol, or tetramethylene glycol.

The amide block polyether block comprises at least one type of polyamide block and one type of polyether block. Mixing two or more polymers with polyamide blocks and polyether blocks may also be used. The amide block polyether also can comprise any amide structure made from the method described on the above.

Preferably, the amide block polyether is such that it represents the major component in weight, i.e., that the amount of polyamide which is under the block configuration and that which is eventually distributed statistically in the chain represents 50 weight percent or more of the amide block polyether. Advantageously, the amount of polyamide and the amount of polyether is in a ratio (polyamide/polyether) of 1/1 to 3/1.

One type of polyetherester elastomer is the family of Pebax, which are available from Elf-AtoChem Company. Preferably, the choice can be made from among Pebax 2533, 3533, 4033, 1205, 7033 and 7233. Blends or combinations of Pebax 2533, 3533, 4033, 1205, 7033 and 7233 can also be prepared, as well. Pebax 2533 has a hardness of about 25 shore D (according to ASTM D-2240), a Flexural Modulus of 2.1 kpsi (according to ASTM D-790), and a Bayshore resilience of about 62% (according to ASTM D-2632). Pebax 3533 has a hardness of about 35 shore D (according to ASTM D-2240), a Flexural Modulus of 2.8 kpsi (according to ASTM D-790), and a Bayshore resilience of about 59% (according to ASTM D-2632). Pebax 7033 has a hardness of about 69 shore D (according to ASTM D-2240) and a Flexural Modulus of 67 kpsi (according to ASTM D-790). Pebax 7333 has a hardness of about 72 shore D (according to ASTM D-2240) and a Flexural Modulus of 107 kpsi (according to ASTM D-790).

Some examples of suitable polyamides for use include those commercially available under the trade names PEBAX, CRISTAMID and RILSAN marketed by Atofina Chemicals of Philadelphia, Pa., GRIVORY and GRILAMID marketed by EMS Chemie of Switzerland, S.L., TROGAMID and VESTAMID available from Degussa, and ZYTEK marketed by E.I. DuPont de Nemours & Co., of Wilmington, Del.

The golf balls may include the traditional rubber components used in golf ball applications including, both natural and synthetic rubbers, such as cis-1,4-polybutadiene, trans-1,4-polybutadiene, 1,2-polybutadiene, cis-polyisoprene, trans-polyisoprene, polycholoroprene, polybutylene, styrene-butadiene rubber, styrene-butadiene-styrene block copolymer and partially and fully hydrogenated equivalents, styrene-isoprene-styrene block copolymer and partially and fully hydrogenated equivalents, nitirile rubber, silicone rubber, and polyurethane, as well as mixtures of these. Polybutadiene rubbers, especially 1,4-polybutadiene rubbers containing at least 40 mol%, and more preferably 80 to 100 mol% of cis-1,4 bonds, are preferred because of their high rebound resilience, moldability, and high strength after vulcanization. The polybutadiene component may be synthesized by using rare earth-based catalysts, nickel-based catalysts, or cobalt-based catalysts, conventionally used in this field. Polybutadiene obtained by using lanthanum rare earth-based catalysts usually employ a combination of a lanthanum rare earth (atomic number of 57 to 71)-compound, but particularly preferred is a neodymium compound.

The 1,4-polybutadiene rubbers have a molecular weight distribution (Mw/Mn) of from about 1.2 to about 4.0, preferably from about 1.7 to about 3.7, even more preferably from about 2.0 to about 3.5, most preferably from about 2.2 to about 3.2. The polybutadiene rubbers have a Mooney viscosity (ML(1+4) (100°C) ) of from about 20 to about 80, preferably from about 30 to about 70, even more preferably from about 30 to about 60, most preferably from about 35 to about 50. The term "Mooney viscosity" used herein refers in each case to an industrial index of viscosity as measured with a Mooney viscometer, which is a type of rotary plastimeter (see JIS K6300). This value is represented by the symbol ML(1+4) (100°C) , wherein "M" stands for Mooney viscosity; "L" stands for large rotor (L-type), "1+4" stands for a pre-heating time of 1 minute and a rotor rotation time of 4 minutes, and "100°C"
indicates that measurement was carried out at a temperature of 100°C. As readily appreciated by one skilled in the art, blends of polybutadiene rubbers may also be utilized in the golf balls of the present invention, such blends may be prepared with any mixture of rare earth-based catalysts, nickel-based catalysts, or cobalt-based catalysts derived materials, and from materials having different molecular weights, molecular weight distributions and Mooney viscosity. [0135] The cores and/or the intermediate layer(s) of the golf balls may also include 1,2-polybutadienes having differing tacticity, all of which are suitable as unsaturated polymers for use in the presently disclosed compositions, are atactic 1,2-polybutadiene, isotactic 1,2-polybutadiene, and syndiotactic 1,2-polybutadiene. Syndiotactic 1,2-polybutadiene having crystallinity suitable for use as an unsaturated polymer in the presently disclosed compositions are polymerized from a 1,2-addition of butadiene. The presently disclosed golf balls may include syndiotactic 1,2-polybutadiene having crystallinity and greater than about 70% of 1,2-bonds, more preferably greater than about 80% of 1,2-bonds, and most preferably greater than about 90% of 1,2-bonds. Also, the 1,2-polybutadiene may have a mean molecular weight between about 10,000 and about 350,000, more preferably between about 50,000 and about 300,000, more preferably between about 80,000 and about 200,000, and most preferably between about 100,000 and about 150,000. Examples of suitable syndiotactic 1,2-polybutadienes having crystallinity suitable for use in golf balls are sold under the trade names RB810, RB820, and RB830 by JSR Corporation of Tokyo, Japan. These have more than 90% of 1,2 bonds, a mean molecular weight of approximately 120,000, and crystallinity between about 15% and about 30%. [0136] The cores and/or the intermediate layer(s) of the golf balls may also include polyalkenamers. Examples of suitable polyalkenamer rubbers are polypentenamer rubber, polyheptenamer rubber, polyoctenamer rubber, polydodecanamer rubber, and polydodecanamer rubber. For further details concerning polyalkenamer rubber, see Rubber Chem. & Tech., Vol. 47, page 511-596, 1974, which is incorporated herein by reference. Polyoctenamer rubbers are commercially available from Huls AG of Marl, Germany, and through its distributor in the U.S., Creano Inc. of Somerset, N.J., and sold under the trademark VESTENAMER®. Two grades of the VESTENAMER® trans-polyoctenamer are commercially available: VESTENAMER 8012 designates a material having a trans-content of approximately 80% (and a cis-content of 20%) with a melting point of approximately 54°C; and VESTENAMER 6212 designates a material having a trans-content of approximately 60% (cis-content of 40%) with a melting point of approximately 30°C. Both of these polymers have a double bond at every eighth carbon atom in the ring. [0137] The polyalkenamer rubbers used in the present disclosure exhibit excellent melt processability above their sharp melting temperatures and exhibit high miscibility with various rubber additives as a major component without deterioration of crystallinity which in turn facilitates injection molding. Thus, unlike synthetic rubbers typically used in golf ball preparation, polyalkenamer-based compounds can be prepared which, are injection moldable. This is disclosed in copending U.S. application Ser. No. 11/335,070, filed on Jan. 18, 2006, in the name of Hyun Kim et al., the entire contents of which are hereby incorporated by reference. [0138] As used herein, the term “injection moldable” as applied to the polyalkenamer rubber or polyalkenamer/polyamide compositions used as described herein refers to a material amenable to use in injection molding apparatus designed for use with typical thermoplastic resins. In one example, the term injection moldable composition as applied to the uncrosslinked polyalkenamer rubbers used in the present disclosure means compositions having a viscosity using a Dynamic Mechanical Analyzer (DMA) and ASTM D4440 at 200°C of less than about 5,000 Pa·sec, preferably less than about 3,000 Pa·sec, more preferably less than about 2,000 Pa·sec and even more preferably less than about 1,000 Pa·sec and a storage modulus (G') at 1 Hz measured using a Dynamic Mechanical Analyzer (DMA) and ASTM D4065, and ASTM D4440, at 25°C, and 1 Hz of greater than about 1×10⁷ dyn/cm², preferably greater than about 1.5×10⁷ dyn/cm², more preferably greater than about 1×10⁸ dyn/cm², and most preferably greater than about 2×10⁸ dyn/cm². [0139] A more preferred composition for use in the golf balls and preferably for use in the golf ball core or intermediate layers is a blend of polyalkenamer and polyamide as also disclosed in copending U.S. application Ser. No. 11/335,070, filed on Jan. 18, 2006, in the name of Hyun Kim et al., the entire contents of which are hereby incorporated by reference. The polyalkenamer/polyamide composition used to prepare the golf ball contains from about 2 to about 90 wt %, preferably from about 5 to about 80 wt %, more preferably from about 7 to 70 wt %, and even more preferably from about 10 to 60 wt % (based on the final weight of the injection moldable composition) of one or more polyalkenamer polymers, particularly polyalkenamers of a cycloalkene having from 5-20, preferably 5-15, and most preferably 5-12 ring carbon atoms. The polyalkenamers may be prepared by ring opening metathesis polymerization of one or more cycloalkenes in the presence of organometallic catalysts as described in U.S. Pat. Nos. 3,492,245, and 3,804,803, the entire contents of both of which are herein incorporated by reference. [0140] The polyalkenamer/polyamide composition used to prepare the golf ball also contains from about 10 to about 98 wt %, preferably from about 20 to about 95 wt %, preferably from about 30 to about 95 wt %, and even more preferably from about 40 to 90 wt % (based on the final weight of the injection moldable composition) of one or more polyamide polymers. [0141] According to certain embodiments, the polyalkenamer/polyamide composition contains at least about 60 wt %, preferably at least about 70%, and more preferably at least about 80 wt % of at least one polyamide, based on the total polymer amount of the layer(s) or core that is made from the polyalkenamer/polyamide composition. In further embodiments, the polyamide ingredient of the polyalkenamer/polyamide composition is the major ingredient of the material used to form at least one component (e.g., the core or inner cover layer) of the golf ball. As used herein “major ingredient” means that the polyamide is present in an amount of at least about 50 wt %, based on the total weight of all of the ingredients in the material. [0142] When synthetic rubbers such as the aforementioned polybutadienes or polyalkenamers and their blends are used in the golf balls they may contain further materials typically often used in rubber formulations including crosslinking agents, co-crosslinking agents, peptizers and accelerators. [0143] Suitable cross-linking agents for use in the golf balls include peroxides, sulfur compounds, or other known chemi-
cal cross-linking agents, as well as mixtures of these. Non-limiting examples of suitable cross-linking agents include primary, secondary, or tertiary aliphatic or aromatic organic peroxides. Peroxides containing more than one peroxo group can be used, such as 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane and 1,4-di(2-tert-butyl peroxisypropyl)benzene. Both symmetrical and asymmetrical peroxides can be used, for example, tert-butyl perbenzoate and tert-butyl cumyl peroxide. Peroxides incorporating carboxyl groups also are suitable. The decomposition of peroxides used as cross-linking agents can be brought about by applying thermal energy, shear, irradiation, reaction with other chemicals, or any combination of these. Both homolytically and heterolytically decomposed peroxide can be used. Non-limiting examples of suitable peroxides include: diacetyl peroxide; di-tert-butyl peroxide; dibenzoyl peroxide; dicumyl peroxide; 2,5-dimethyl-2,5-di(benzoyl peroxy)hexane; 1,4-bis(t-butylperoxyisopropyl)benzene; t-butylperoxybenzoe; 2,5-dimethyl-2,5-di(t-butylperoxy)hexene-3, such as Trigonox 145-45B, marketed by Akrochem Corp. of Akron, Ohio; 1,1-bis(t-butyleroxy)-3,3,5-trimethylcyclohexane, such as Varox 231- XL, marketed by R.T. Vanderbilt Co., Inc. of Norwalk, Conn.; and di-(2,4-dichlorobenzoyl) peroxide. The cross-linking agents can be blended in total amounts of about 0.05 part to about 5 parts, more preferably about 0.2 part to about 3 parts, and most preferably about 0.2 part to about 2 parts, by weight of the cross-linking agents per 100 parts by weight of the unsaturated polymer.

Each cross-linking agent has a characteristic decomposition temperature at which 50% of the cross-linking agent has decomposed when subjected to that temperature for a specified time period (t_{1/2}). For example, 1,1-bis-(t-butyleroxy)-3,3,5-trimethylcyclohexane at t_{1/2} = 0.1 hr has a decomposition temperature of 138°C and 2,5-dimethyl-2,5-di-(t-butyleroxy)hexene-3 at t_{1/2} = 0.1 hr has a decomposition temperature of 182°C. Two or more cross-linking agents having different characteristic decomposition temperatures at the same t_{1/2} may be blended in the composition. For example, where at least one cross-linking agent has a first characteristic decomposition temperature less than 150°C, and at least one cross-linking agent has a second characteristic decomposition temperature greater than 150°C, the composition having at least one cross-linking agent having the first characteristic decomposition temperature to the at least one cross-linking agent having the second characteristic decomposition temperature can range from 5:95 to 95:5, or more preferably from 10:90 to 50:50.

Besides the use of chemical cross-linking agents, exposure of the composition to radiation also can serve as a cross-linking agent. Radiation can be applied to the unsaturated polymer mixture by any known method, including using microwave or gamma radiation, or an electron beam device. Additives may also be used to improve radiation curing of the diene polymer.

The rubber and cross-linking agent may be blended with a co-cross-linking agent, which may be a metal salt of an unsaturated carboxylic acid. Examples of these include zinc and magnesium salts of unsaturated fatty acids having 3 to 8 carbon atoms, such as acrylic acid, methacrylic acid, maleic acid, and fumic acid, palmitic acid with the zinc salts of acrylic and methacrylic acid being most preferred. The unsaturated carboxylic acid metal salt can be blended in a rubber either as a preformed metal salt, or by introducing an α,β-unsaturated carboxylic acid and a metal oxide or hydroxide into the rubber composition, and allowing them to react in the rubber composition to form a metal salt. The unsaturated carboxylic acid metal salt can be blended in any desired amount, but preferably in amounts of about 10 parts to about 60 parts by weight of the unsaturated carboxylic acid per 100 parts by weight of the synthetic rubber.

The core compositions may also incorporate one or more of the so-called "peptizers".

The peptizer preferably comprises an organic sulfur compound and/or its metal or non-metal salt. Examples of such organic sulfur compounds include thiophenols, such as pentachlorothiophenol, 4-butyl-3-thiophenol, 4,4’-dithio-benzamide, and 2-benzamidothiophenol; thiocarboxylic acids, such as thiobenzoic acid; 4,4’-dithio dimorpholine; and, sulfides, such as dithiyl disulfide, dibenzoyl disulfide; dibenzothiazyl disulfide; di (pentachlorophenyl) disulfide; dibenzamido diphenyl disulfide (DBDPP), and alkylated phenol sulfides, such as VUL-TAC marketed by Atosina Chemicals, Inc. of Philadelphia, Pa. Preferred organic sulfur compounds include pentachlorothiophenol, and dibenzamido diphenyl disulfide.

Examples of the metal salt of an organic sulfur compound include sodium, potassium, lithium, magnesium calcium, barium, cesium and zinc salts of the above-mentioned thiophenols and thiocarboxylic acids, with the zinc salt of pentachlorothiophenol being most preferred.

Examples of the non-metal salt of an organic sulfur compound include ammonium salts of the above-mentioned thiophenols and thiocarboxylic acids wherein the ammonium cation has the general formula [NR^1R^2R^3R^4]^+ where R^1, R^2, R^3, and R^4 are selected from the group consisting of hydrogen, a C1-C3 aliphatic cycloaliphatic or aromatic moiety, and any and all combinations thereof, with the most preferred being the NH_4^+-salt of pentachlorothiophenol.

Additional peptizers include aromatic or conjugated peptizers comprising one or more heteroatoms, such as nitrogen, oxygen and/or sulfur. More typically, such peptizers are heteroary or heterocyclic compounds having at least one heteroatom, and potentially plural heteroatoms, where the plural heteroatoms may be the same or different. Such peptizers include peptizers such as an indole peptizer, a quinoline peptizer, an isoquinoline peptizer, a pyridine peptizer, a pyrrole peptizer, a pyridazine peptizer, a pyrazine peptizer, a triazine peptizer, a carbazole peptizer, or combinations of such peptizers.

Suitable peptizers also may include one or more additional functional groups, such as halogens, particularly chlorine; a sulfur-containing moiety exemplified by thiols, where the functional group is sulfhydryl (—SH), thioethers, where the functional group is —SR, disulfides, (R,S—SR), etc.; and combinations of functional groups. Such peptizers are more fully disclosed in copending U.S. application Ser. No. 60/752,475 filed on Dec. 20, 2005 in the name of Hyun Kim et al, the entire contents of which are herein incorporated by reference.

The peptizer, if employed in the golf balls of the present invention, is present in an amount up to about 10, from about 0.01 to about 10, preferably of from about 0.1 to about 7, more preferably of from about 0.15 to about 5 parts by weight per 100 parts by weight of the synthetic rubber component.

The core compositions can also comprise one or more accelerators of one or more classes. Accelerators are added to an unsaturated polymer to increase the vulcanization
rate and/or decrease the vulcanization temperature. Accelerators can be of any class known for rubber processing including mercapto-, sulenamide-, thiram, dithiocarbamate, dithiocarbamyl-sulfenamide, xanthate, guanidine, amine, thiourea, and dithiophosphate accelerators. Specific commercial accelerators include 2-mercaptobenzothiazole and its metal or non-metal salts, such as Vulkacet Mercapto C, Mercapto MGC, Mercapto ZM-5, and ZM marketed by Bayer AG of Leverkusen, Germany, Nocceler M, Nocceler MZ, and Nocceler M-60 marketed by Ouchi-Mirko Chemical Industrial Company, Ltd. of Tokyo, Japan, and MBT and ZMBT marketed by Akrochem Corporation of Akron, Ohio. A more complete list of commercially available accelerators is given in The Vanderbilt Rubber Handbook: 13th Edition (1990, R.T. Vanderbilt Co.), pp. 296-330, in Encyclopedia of Polymer Science and Technology, Vol. 12 (1970, John Wiley & Sons), pp. 258-259, and in Rubber Technology Handbook (1980, Hanser/Gardner Publications), pp. 234-236. Preferred accelerators include 2-mercaptopbenzothiazole (MBT) and its salts. The synthetic rubber composition can further incorporate from about 0.1 part to about 10 parts by weight of the accelerator per 100 parts by weight of the rubber. More preferably, the ball composition can further incorporate from about 0.2 part to about 5 parts, and most preferably from about 0.5 part to about 1.5 parts, by weight of the accelerator per 100 parts by weight of the rubber. The polymeric compositions used to prepare the golf balls also can incorporate one or more fillers. Such fillers are typically in a finely divided form, for example, in a size generally less than about 20 mesh, preferably less than about 100 mesh U.S. standard size, except for fibers and flock, which are generally elongated. Filler particle size will depend upon desired effect, cost, ease of addition, and dusting considerations. The appropriate amounts of filler required will vary depending on the application but typically can be readily determined without undue experimentation.

The filler preferably is selected from the group consisting of precipitated hydrated silica, limestone, clay, talc, asbestos, barytes, glass fibers, aramid fibers, mica, calcium metasilicate, barium sulfate, zinc sulfide, lithopone, silicates, silicon carbide, diatomaceous earth, carbonates such as calcium or magnesium or barium carbonate, sulfates such as calcium or magnesium or barium sulfate, metals, including tungsten, steel, copper, cobalt or iron, metal alloys, tungsten carbide, metal oxides, metal steatites, and other particulate carbonaceous materials, and any and all combinations thereof. Preferred examples of fillers include metal oxides, such as zinc oxide and magnesium oxide. In another preferred embodiment, the filler comprises a continuous or non-continuous fiber. In another preferred embodiment, the filler comprises one or more so-called nano-fillers, as described in U.S. Pat. No. 6,794,447 and copending U.S. patent application Ser. No. 10/670,090 filed on Sep. 24, 2003 and copending U.S. patent application Ser. No. 10/926,509 filed on Aug. 25, 2004, the entire contents of each of which are incorporated herein by reference.

Inorganic nano-filler material generally is made of clay, such as hydrotalcite, phylloclasticite, saponite, hectorite, beidellite, stevensite, vermiculite, halloysite, mica, montmorillonite, micaceous, or octosilicate. To facilitate incorporation of the nano-filler material into a polymer material, either in preparing nanocomposite materials or in preparing polymer-based golf ball compositions, the clay particles generally are coated or treated by a suitable compatibilizing agent. The compatibilizing agent allows for superior linkage between the inorganic and organic material, and it also can account for the hydrophilic nature of the inorganic nano-filler material and the possibly hydrophobic nature of the polymer.Compatibilizing agents may exhibit a variety of different structures depending upon the nature of both the inorganic nano-filler material and the target matrix polymer. Non-limiting examples include hydroxy-, thiol-, amino-, epoxy-, carboxylic acid-, ester-, amide-, and siloxy-group containing compounds, oligomers or polymers. The nano-filler materials can be incorporated into the polymer either by dispersion into the particular monomer or oligomer prior to polymerization, or by melt compounding of the particles either in the matrix polymer. Examples of commercial nanofillers are various Cloisite grades including 10A, 15A, 20A, 25A, 30B, and NA of Southern Clay Products (Gonzales, Tex.) and the Nanomer grades including 1.24TL and C.30EVA of Nanocor, Inc. (Arlington Heights, Ill.).

Nano-fillers when added into a matrix polymer, such as the polyelektamer rubber, can be mixed in three ways. In one type of mixing there is dispersion of the aggregate structures within the matrix polymer, but on mixing no interaction of the matrix polymer with the aggregate platelet structure occurs, and thus the stacked platelet structure is essentially maintained. As herein, this type of mixing is defined as “undispersed”.

However, if the nano-filler material is selected correctly, the matrix polymer chains can penetrate into the aggregates and separate the platelets, and thus when viewed by transmission electron microscopy or x-ray diffraction, the aggregates of platelets are expanded. At this point the nanofiller is said to be substantially evenly dispersed within and reacted into the structure of the matrix polymer. This level of expansion can occur to differing degrees. If small amounts of the matrix polymer are layered between the individual platelets then, as used herein, this type of mixing is known as “intercalation”.

In some circumstances, further penetration of the matrix polymer chains into the aggregate structure separates the platelets, and leads to a complete disruption of the platelet’s stacked structure in the aggregate. Thus, when viewed by transmission electron microscopy (TEM), the individual platelets are thoroughly mixed throughout the matrix polymer. As used herein, this type of mixing is known as “exfoliated”. An exfoliated nano-filler has the platelets fully dispersed throughout the polymer matrix; the platelets may be dispersed unevenly but preferably are dispersed evenly.

While not wishing to be limited to any theory, one possible explanation of the differing degrees of dispersion of such nano-fillers within the matrix polymer structure is the effect of the compatibilizer surface coating on the interaction between the nano-filler platelet structure and the matrix polymer. By careful selection of the nano-filler it is possible to vary the penetration of the matrix polymer into the platelet structure of the nano-filler on mixing. Thus, the degree of interaction and intrusion of the polymer matrix into the nano-filler controls the separation and dispersion of the individual platelets of the nano-filler within the polymer matrix. This interaction of the polymer matrix and the platelet structure of the nano-filler is defined herein as the nano-filler “reacting into the structure of the polymer” and the subsequent dispersion of the platelets within the polymer matrix is defined herein as the nano-filler “being substantially evenly dispersed” within the structure of the polymer matrix.
If no compatibilizer is present on the surface of a filler such as a clay, or if the coating of the clay is attempted after its addition to the polymer matrix, then the penetration of the matrix polymer into the nanofiller is much less efficient, very little separation and no dispersion of the individual clay platelets occurs within the matrix polymer.

Physical properties of the polymer will change with the addition of nanofiller. The physical properties of the polymer are expected to improve even more as the nanofiller is dispersed into the polymer matrix to form a nanocomposite.

Materials incorporating nanofiller materials can provide these property improvements at much lower densities than those incorporating conventional fillers. For example, a nylon-6 nanocomposite material manufactured by RTP Corporation of Wichita, Kans., uses a 3% to 5% clay loading and has a tensile strength of 11,800 psi and a specific gravity of 1.14, while a conventional 30% mineral-filled material has a tensile strength of 8,000 psi and a specific gravity of 1.36. Using nanocomposite materials with lower inorganic materials loadings than conventional fillers provides the same properties, and this allows products comprising nanocomposite fillers to be lighter than those with conventional fillers, while maintaining those same properties.

Nanocomposite materials are materials incorporating up to about 20%, or from about 0.1% to about 20%, preferably from about 0.1% to about 15%, and most preferably from about 0.1% to about 10% of nanofiller reacted into and substantially dispersed through intercalation or exfoliation into the structure of an organic material, such as a polymer, to provide strength, temperature resistance, and other property improvements to the resulting composite. Descriptions of particular nanocomposite materials and their manufacture can be found in U.S. Pat. No. 5,962,553 to Ellsworth, U.S. Pat. No. 5,385,776 to Maxfield et al., and U.S. Pat. No. 4,894,411 to Okada et al. Examples of nanocomposite materials currently marketed include M1030D, manufactured by UNITIKI Limited, of Osaka, Japan, and 105C2, manufactured by UBE America of New York, N.Y.

When nanocomposites are blended with other polymer systems, the nanocomposite may be considered a type of nanofiller concentrate. However, a nanofiller concentrate may be more generally a polymer into which nanofiller is mixed; a nanofiller concentrate does not require that the nanofiller has reacted and/or dispersed evenly into the carrier polymer.

For the polyalkenamers, the nanofiller material is added in an amount up to about 20 wt%, from about 0.1% to about 20%, preferably from about 0.1% to about 15%, and most preferably from about 0.1% to about 10% by weight (based on the final weight of the polymer matrix material) of nanofiller reacted into and substantially dispersed through intercalation or exfoliation into the structure of the core polymer matrix.

If desired, the various polymer compositions used to prepare the golf balls can additionally contain other conventional additives such as plasticizers, pigments, antioxidants, U.V. absorbers, optical brighteners, or any other additives generally employed in plastics formulation or the preparation of golf balls.

Another particularly well-suited additive includes compounds having the general formula:

\[ (R_2N)_n - R - (\text{X}(O)\text{R}_2)_m \]

where \( R \) is hydrogen, or a \( \text{C}_1-\text{C}_{20} \) aliphatic, cycloaliphatic or aromatic system; \( R' \) is a bridging group comprising one or more \( \text{C}_1-\text{C}_{20} \) straight chain or branched aliphatic or alicyclic groups, or substituted straight chain or branched aliphatic or alicyclic groups, or aromatic group, or an oligomer of up to 12 repeating units including, but not limited to, polypeptides derived from an amino acid sequence of up to 12 amino acids; and \( X \) is O or S or P with the proviso that when \( X = C \), \( n = 1 \) and \( y = 1 \) and when \( X = S \), \( n = 2 \) and \( y = 1 \), and when \( X = P \), \( n = 2 \) and \( y = 2 \). Also, \( m = 1-3 \). These materials are more fully described in copending U.S. patent application Ser. No. 11/182,170, filed on Jul. 14, 2005, the entire contents of which are incorporated herein by reference. These materials include, without limitation, caprolactam, oenanthoactam, decanolactam, undecanolactam, dodecanolactam, caproic 6-amino acid, 11-aminoundecanoic acid, 12-amino:dodecanoic acid, diaminohexamethylene salts of adipic acid, azelaic acid, sebacic acid and 1,12-dodecanedioic acid and the diamine nonamethylenesalt of adipic acid, 2-amino: nicnamic acid, 1-:aspartic acid, 5-aminosalicylic acid, aminobutyric acid; aminocaproic acid; aminocaproic acid; 1-aminocarboxylato-1-cyclopropane: borne dicarboxylic acid; aminocephalosporanic acid; aminobenzoic acid; aminochlorobenzoic acid; 2-(3-amino-4-chlorobenzoyl)benzoic acid; aminomphatic acid; amononcorrtnic acid; aminonic: nicillic acid; aminopentenonic acid; (aminophenyl) butyric acid; aminophenyl propionic acid; aminopropionic acid; aminofolic acid; aminopyrazine carboxylic acid; aminopyrazole carboxylic acid; aminoverh: niclylic acid; aminoterephthalic acid; aminovaleric acid; ammonium hydrogen: carbamate; anthranilic acid; aminobenzenophenone carboxylic acid; aminoucinnamic acid, epsilon-caprolactam; omega-caprolactam, (carboxy: methyl)acetic acid, sodium salt; carbenzyloxy aspartic acid; carboxamidyl aspartic acid; carboxy:loxy glycine; 2-aminoethyl hydrogensulfate; amonanphthalamenesulfonic acid; aminotoluene sulfonic acid; 4,4'-methylen: bis-(cylohexylamine)carbamate and ammonium carbamate.

Most preferably the material is selected from the group consisting of 4,4'-methylen: bis-(cylohexylamine)carbamate (commercially available from R T. Vanderbilt Co., Norwalk Conn. under the tradename Diakote-4), 11-aminoundecan: decanonic acid, 12-amino: dodecanoic acid, epsilon-caprolactam; omega-caprolactam; and any and all combinations thereof.

In an especially preferred embodiment a nanofiller additive component in the golf balls is surface modified with a compatibilizing agent comprising the earlier described compounds having the general formula:

\[ (R_2N)_n - R' - (\text{X}(O)\text{R}_2)_m \]

A most preferred embodiment would be a filler comprising a nanofiller clay material surface modified with an amino acid including 12-amino: dodecanoic acid. Such fillers are available from Nanomex Co. under the tradename Nanomer 1.24TL.

The filler can be blended in variable effective amounts, such as amounts of greater than 0 to at least about 80 parts, and more typically from about 10 parts to about 80 parts, by weight per 100 parts by weight of the base rubber. If desired, the rubber composition can additionally contain effective amounts of a plasticizer, an antioxidant, and any other additives generally used to make golf balls.
Various compositions used as a component of the golf balls may also comprise a monomeric amide or modifiers, such as a monomeric aliphatic and/or aromatic amide polymer modifier or modifiers. An amide is any organic compound containing the group —CONR₂, where R is hydrogen; an aliphatic group, such as an alkyl group, an alkenyl group, or an alkynyl group; an aromatic group; and combinations thereof. Amides useful for the present invention may be a primary amide, a secondary amide, or a tertiary amide, and combinations thereof; i.e., a particular compound may have two or more amide moieties where one of the amide moieties is a primary, secondary or tertiary amide and the other amide moiety has a degree of substitution different from the first amide moiety. For example, if the first amide is a primary amide, the second amide moiety may be secondary or tertiary.

The amide may be saturated or unsaturated. Moreover, unsaturated amides may have more than one site of unsaturation, including aromatic amides. Alkene amides may have a cis double bond or a trans double bond. For compounds having plural sites of unsaturation, such double bonds can be all cis, all trans, or any combination of cis and trans double bonds. Certain compounds perform better as polymer modifiers if the olefin is entirely or predominantly cis, or entirely or predominantly trans. Moreover, the position of the double bond in the compound may affect the compound's usefulness for modifying polymer compositions.

Amidated aliphatic and/or aromatic compounds typically have from about 1 to about 100 carbon atoms, more typically from about 2 to about 80 carbon atoms, even more typically from about 5 to about 50 carbon atoms, even more typically from about 5 to about 30 carbon atoms, and most typically from about 10 to about 25 carbon atoms.

Fatty acid amides are a particularly useful genus of amides. Fatty acids are any of a class of aliphatic monocarboxylic acids that form part of a lipid molecule and can be derived from fat by hydrolysis; fatty acids are simple molecules built around a series of carbon atoms linked together in a chain, typically a chain having from about 12 to 22 carbon atoms.

Particular examples of amides include, without limitation, primary amides, such as stearamide, behenamide, oleamide, and erucamide; secondary amides, such as stearyl erucamide, erucyl erucamide, oleyl palmitamide, stearyl stearamide, and the like; unsaturated, such as N,N'-ethylenbisstearamide, N,N'-ethylenbisoleamide, and the like; amidated natural waxes, such as camellia wax amide, rice wax amide, montan wax amide, and the like; and combinations of any two or more of any suitable amide.

Suitable amide polymer composition modifiers can include a functional group or groups other than the amide functionality. For example and without limitation, amide polymer modifiers also can include additional functional groups such as hydroxyl, sulfhydryl, halides, glycercidyl, carboxyl, carboxyl, anhydryl, ether, epoxide, amine, etc., and combinations of all such functional groups.

The polymer compositions include amounts of the amide modifying agent effective to modify the compositions as desired. For example, amide modifiers can be used to provide more desirable rheological properties relative to non-modified polymeric compositions, more desirable mechanical properties relative to non-modified polymeric compositions, and combinations of rheological and mechanical properties. By way of example, it was surprising to find that useful polymeric compositions modified with a suitable monomeric amide, or amides, could be made such that the rheological properties, for example the melt flow index (MFI), could be advantageously modified. At the same time, mechanical properties, such as hardness, flexural modulus, and COR, could be substantially maintained, and for some formulations improved, relative to the same composition without the monomeric amide, or amides. It was particularly surprising that useful amounts of modifying agents could be increased to relatively high concentrations, such as 1% by weight or greater, to modify certain polymer properties advantageously while maintaining suitable COR values.

By way of example and without limitation, it currently is believed that amide modifiers can be added in amounts ranging from about 0.1 to about 50 parts per hundred (pph), more typically from about 0.1 to about 20 pph, more typically from about 0.5 pph to about 15 pph, and most typically from about 1 to about 10 pph, based on the weight of the polymeric portion of the composition.

Golf balls also can include, in suitable amounts, one or more additional ingredients generally employed in golf ball compositions. Agents provided to achieve specific functions, such as additives and stabilizers, can be present. Example suitable ingredients include colorants, antioxidants, colorants, dispersants, mold releasing agents, processing aids, fillers, and any and all combinations thereof. Although not required, UV stabilizers, or photo stabilizers such as substituted hydroxyphenyl benzotriazoles may be utilized to enhance the UV stability of the final compositions. An example of a commercially available UV stabilizer is the stabilizer sold by Ciba Geigy Corporation under the tradename TINUVIN.

Typically, the golf ball core is made by mixing together the various components and other additives with or without melting them. Dry blending equipment, such as a tumbling mixer, V-blender, ribbon blender, or two-roll mill, can be used to mix the compositions. The golf ball compositions can be also be mixed using a mill, internal mixer such as a Banbury or Farrel continuous mixer, extruder or combinations of these, with or without application of thermal energy to produce melting. The various core components can be mixed together with the cross-linking agents, or each additive can be added in an appropriate sequence to the milled unsaturated polymer. In another method of manufacture the cross-linking agents and other components can be added to the unsaturated polymer as part of a concentrate using dry blending, roll milling, or melt mixing. If radiation is a cross-linking agent, then the mixture comprising the unsaturated polymer and other additives can be irradiated following mixing, during forming into a part such as the core of a ball, or after forming.

The resulting mixture can be subjected to, for example, a compression or injection molding process, to obtain solid spheres for the core. The polymer mixture is subjected to a molding cycle in which heat and pressure are applied while the mixture is confined within a mold. The cavity shape depends on the portion of the golf ball being formed. The compression and heat liberates the free radicals by decomposing one or more peroxides, which initiate cross-linking. The temperature and duration of the molding cycle are selected based upon the type of peroxide and peptizer selected. The molding cycle may have a single step of molding the mixture at a single temperature for fixed time duration. For example, a preferred mode of preparation for the cores is to first mix the core ingredients on a two-roll mill to form slugs of approximately 30-40 g and then compression mold in a single step at a temperature between 150 to 180°C. for times between 5 and 12 minutes.
The various core components may also be combined to form a golf ball by an injection molding process, which is also well known to one of ordinary skill in the art. Although the curing time depends on the various materials selected, those of ordinary skill in the art will be readily able to adjust the curing time upward or downward based on the particular materials used and the discussion herein.

Conventionally, golf ball cover and intermediate layers are positioned over a core or other internal layer using one of three methods: casting, injection molding, or compression molding.

Injection molding generally involves using a mold having one or more sets of two hemispherical mold sections that mate to form a spherical cavity during the molding process. The pairs of mold sections are configured to define a spherical cavity in their interior when mated. When used to mold an outer cover layer for a golf ball, the mold sections can be configured so that the inner surfaces that mate to form the spherical cavity include protrusions configured to form dimples on the outer surface of the molded cover layer. The mold sections are connected to openings, or gates, evenly distributed near or around the parting line, or point of intersection, of the mold sections through which the material to be molded flows into the cavity. The gates are connected to a runner and a sprue that serve to channel the molding material through the gates. When used to mold a layer onto an existing structure, such as a ball core, the mold includes a number of support pins disposed throughout the mold sections. The support pins are configured to be retractable, moving into and out of the cavity perpendicular to the spherical cavity surface. The support pins maintain the position of the core while the molten material flows through the gates into the cavity between the core and the mold sections. The mold itself may be a cold mold or a heated mold. In the case of a heated mold, thermal energy is applied to the material in the mold so that a chemical reaction may take place in the material. Because thermoset materials have desirable mechanical properties, it would be beneficial to producers of golf balls using this process.

Unfortunately, thermoset materials generally are not well suited for injection molding, because as the reactants for thermoset polyurethane are mixed, they begin to cure and become highly viscous while traveling through the sprue and into the runners of the injection mold, leading to injection difficulties. For this reason, thermoset materials typically are formed into a ball layer using a casting process free of any injection molding steps.

In contrast to injection molding, which generally is used to prepare layers from thermoplastic materials, casting often is used to prepare layers from thermoset material (i.e., materials that cure irreversibly). In a casting process, the thermoset material is added directly to the mold sections immediately after it is created. Then, the material is allowed to partially cure to a gelatinous state, so that it will support the weight of a core. Once cured to this state, the core is positioned in one of the mold sections, and the two mold sections are then mated. The material then cures to completion, forming a layer around the core. The timing of the positioning of the core is crucial for forming a layer having uniform thickness. The equipment used for this positioning is costly, because the core must be centered in the material in its gelatinous state, and at least one of the mold sections, after having material positioned therein, must be turned over and positioned onto its corresponding mold section.

Compression molding of a ball layer typically requires the initial step of making half shells by injection molding the layer material into a cold injection mold. The half shells then are positioned in a compression mold around a ball core, whereupon heat and pressure are used to mold the half shells into a complete layer over the core.

Compression molding also can be used as a curing step after injection molding. In such a process, an outer layer of thermally curable material is injection molded around a core in a cold mold. After the material solidifies, the ball is removed and placed into a mold, in which heat and pressure are applied to the ball to induce curing in the outer layer.

Reaction injection molding is a processing technique used specifically for certain reactive thermosetting plastics. As mentioned above, by “reactive” it is meant that the polymer is formed from two or more components which react. Generally, the components, prior to reacting, exhibit relatively low viscosities. The low viscosities of the components allow the use of lower temperatures and pressures than those utilized in traditional injection molding. In reaction injection molding, the two or more components are combined and reacted to produce the final polymerized material. Mixing of these separate components is critical, a distinct difference from traditional injection molding. The process of reaction injection molding a golf ball cover involves placing a golf ball core into a die, closing the die, injecting the reactive components into a mixing chamber where they combine, and transferring the combined material into the die. The mixing begins the polymerization reaction which is typically completed upon cooling of the cover material.

Finally, the mold material itself and any supporting pins and vent pins may be made at least in part from a porous metal material. The porous metal is suitable for use as part of an injection or compression mold. The porous metal can be used for all or part of the mold sections defining the spherical cavity. Other regions of the mold that can advantageously be made from porous metal include pins, runners, sprues, and any other parts of the mold which come in contact with the material from which the ball portions are formed. Full details of this mold design are disclosed in U.S. Pat. No. 6,776,942 to H. J. Kim, the entire contents of which are herein incorporated by reference. The various intermediate layer and/or cover formulations may be produced using a twin-screw extruder or can be blended manually or mechanically prior to the addition to the injection mold or feeder hopper.

Referring to the drawing in FIG. 2 there is illustrated a 3-piece golf ball comprising a core, an intermediate layer, and an outer cover layer. Golf balls also typically include plum dimples formed in the outer cover layer and arranged in various desired patterns.

The core of the multi-piece golf balls may have a diameter of from about 0.5 to about 1.62, preferably from about 0.7 to about 1.60, more preferably from about 1 to about 1.58 inches.

The core of the multi-piece golf balls may have a PGA compression of from about 10 to about 100, preferably from about 35 to about 90, more preferably from about 40 to about 80.

The core of the golf balls may also comprise a center and one or more core layers disposed around the center. These core layers may be made from the same rubber as used in the center portion, or may be a different thermoplastic elastomer. The various core layers (including the center) may each exhibit a different hardness. The difference between the cen-
ter hardness and that of the next adjacent layer, as well as the difference in hardness between the various core layers is greater than 2, preferably greater than 5, most preferably greater than 10 units of Shore D.

In one preferred embodiment, the hardness of the center and each sequential layer increases progressively outwards from the center to outer core layer.

In another preferred embodiment, the hardness of the center and each sequential layer decreases progressively inwards from the outer core layer to the center.

The intermediate layers of the multi-piece golf balls may have a thickness of about 0.01 to about 0.50, preferably from about 0.02 to about 0.30 or more preferably from about 0.03 to about 0.20 or most preferably from about 0.03 to about 0.10 in.

The intermediate layers of the multi-piece golf balls may have a hardness greater than about 25, preferably greater than about 30, more preferably greater than about 40, and most preferably greater than about 50, Shore D units as measured on the ball.

The intermediate layers of the multi-piece golf balls may have a flexural modulus from about 5 to about 500, preferably from about 15 to about 400, more preferably from about 20 to about 300, still more preferably from about 25 to about 200, and most preferably from about 30 to about 150 kpsi.

The cover of the multi-piece golf balls may have a thickness of from about 0.01 to about 0.20 inch, preferably from about 0.02 to about 0.15 inch, more preferably from about 0.03 to about 0.10 inch and most preferably from about 0.03 to about 0.07 inches.

The cover of the multi-piece golf balls also may have a hardness of from about 25 to about 80, more preferably from about 30 to about 70, even more preferably from about 40 to about 60 Shore D.

According to certain embodiments, polyurethane, polyurea, or a combination thereof constitutes the majority (for example, greater than 50 wt. %, particularly greater than 75 wt. %, and more particularly greater than 90 wt. %) polymer present in the cover. According to certain embodiments, the cover is substantially free of an ionomer.

The multi-piece golf balls may have a PGA ball compression greater than about 30, preferably greater than about 40, more preferably greater than about 50, most preferably greater than about 60.

Although FIGS. 1 and 2 illustrate only two- and three-piece golf ball constructions, golf balls may comprise from 0 to at least 5 intermediate layer(s), preferably from 0 to 3 intermediate layer(s), more preferably from 1 to 3 intermediate layer(s), and most preferably 1 to 2 intermediate layer(s).

In certain illustrative embodiments, the multi-piece golf balls also have a Sound Pressure Level, S, of less than 81.5 dB, preferably less than 81 dB, even more preferably less than 80.5.

In certain illustrative embodiments, the multi-piece golf balls of the present invention also have a Sound Pressure Level, S, which meets the following inequality:

\[ S_e < 0.032143F + 189.5 \]

and preferably meets the following inequality:

\[ S_e < 0.010000F + 112.0 \]

where \( F \) is the golf ball frequency in Hz.

The COR of the multi-piece golf balls may be greater than about 0.760, preferably greater than about 0.780, more preferably greater than 0.790, most preferably greater than 0.795, and especially greater than 0.800 at 125 ft/sec inbound velocity.

The COR of the multi-piece golf balls may also be greater than about 0.760, preferably greater than about 0.780, more preferably greater than 0.790, most preferably greater than 0.795, and especially greater than 0.800 at 143 ft/sec inbound velocity.

In illustrative embodiments, the golf ball includes:

- a low PGA compression core (for example, a PGA compression of 40 to 80, preferably a PGA compression of less than 60), preferably the core includes at least one nanocomposite and/or nanofiller;
- at least one intermediate layer comprising a poly-alkenamer, preferably a crosslinked polyalkenamer; and
- a polyurethane cover, preferably a cast polyurethane cover.

EXAMPLES

The following examples are provided to illustrate certain features of embodiments of the disclosed golf balls. A person of ordinary skill in the art will appreciate that the invention is not limited to those features exemplified by these examples.

PGA compression, C.O.R., and Shore D hardness were conducted on materials and/or golf balls made according to the present disclosure using the test methods as defined below.

Shore D hardness was measured in accordance with ASTM D2240. Hardness of a layer was measured on the ball, perpendicular to a land area between the dimples. Core or ball diameter was determined using standard linear calipers or a standard size gauge.

Compression is measured by applying a spring-loaded force to the sphere to be examined, with a manual instrument (an “Attie gauge”) manufactured by the Atti Engineering Company of Union City, N.J. This machine, equipped with a Federal Dial Gauge, Model DB1-C, employs a calibrated spring under a known load. The sphere to be tested is forced a distance of 0.2 inch (5 mm) against this spring. If the spring, in turn, compresses 0.2 inch, the compression is rated at 100; if the spring compresses 0.1 inch, the compression value is rated as 0. Thus more compressible, softer materials will have lower Attie gauge values than harder, less compressible materials. The value is taken shortly after applying the force and within at least 5 secs if possible. Compression measured with this instrument is also referred to as PGA compression.

The approximate relationship that exists between Attie or PGA compression and Riehle compression can be expressed as:

\( \text{Attie or PGA compression} = \frac{160}{100 - \text{Riehle compression}} \)

Thus, a Riehle compression of 100 would be the same as an Attie compression of 60.

The initial velocity of a golf ball after impact with a golf club is governed by the United States Golf Association (“USGA”). The USGA requires that a regulation golf ball can have an initial velocity of no more than 250 feet per second ±2% or 255 feet per second. The USGA initial velocity limit is related to the ultimate distance that a ball may travel (280
yards±6%), and is also related to the coefficient of restitution ("COR"). The coefficient of restitution is the ratio of the relative velocity between two objects after direct impact to the relative velocity before impact. As a result, the COR can vary from 0 to 1, with 1 being equivalent to a completely elastic collision and 0 being equivalent to a completely inelastic collision. Since a ball’s COR directly influences the ball’s initial velocity after club collision and travel distance, golf ball manufacturers are interested in this characteristic for designing and testing golf balls.

[0220] Golf ball Sound Pressure Level, S, in decibels (dB) and Frequency in hertz (Hz) was measured by dropping the ball from a height of 113 in onto a marble ("starnet crystal pink") stage of at least 12" square and 4.25 inches in thickness. The sound of the resulting impact was captured by a microphone positioned at a fixed proximity of 12 inches, and at an angle of 30 degrees from horizontal, from the impact position and resolved by software transformation into an intensity in db and a frequency in Hz. Data collection was done as follows:

[0221] Microphone data is collected using a laptop PC with a sound card. An A-weighting filter is applied to the analog signal from the microphone. This signal is then digitally sampled at 44.1 kHz by the laptop data acquisition system for further processing and analysis. Data Analysis was done as follows:

[0222] The data analysis is split into two processes:

[0223] a. Time series analysis that generates the root mean square (rms) sound pressure level (SPL) for each ball impact sound.

[0224] i. An rms SPL from a reference calibration signal is generated in the same manner as the ball data.

[0225] ii. The overall SPL (in decibels) is calculated from the reference signal for each ball impact sound.

[0226] iii. The median SPL is recorded based on 3 impact tests.

[0227] b. Spectral analyses for each ball impact sound

[0228] i. Fourier and Autoregressive spectral estimation techniques are employed to create power spectra.

[0229] ii. The frequencies (in cycles/sec-HZ) from highest level peaks representing the most active sound producing vibration modes of each ball are identified.

Example 1

Ball Preparation

[0230] A solid core was prepared, having a diameters of 1.510 inches and incorporating as the base rubber, cis-1,4-polybutadiene made with a rare earth catalyst. The core also incorporated rubber grade zinc oxide purchased from Akrochem (Akron, Ohio), zinc diacrylate, "ZDA" commercially available from Sartomer as well as a peroxide cross-linking initiator. The core ingredients were mixed on a two-roll mill, and slugs of approximately 34.5 g were formed and compression-molded at 170° C., for seven minutes. The resulting core had a PGA compression of 60 as measured after one day of aging at room temperature.

[0231] A mantle material was made from a blend of two copolymeric ionomers each having an acid content of greater than 16 wt.%, was then injection molded around the core to a thickness of 0.055 in to yield a mantle core having a Shore D hardness as measured on the curved surface thereof of 66D. A finished golf ball was then prepared by casting a thermost urethane cover around the mantled core to produce a golf ball with a dimpled surface and of 1.680 inches in diameter having the ball constructions and properties as summarized in Table 1. The thermost polyurethane cover was made from Chemtura LP950A (a toluene disocyanate urethane prepolymer) and ETHACURE E1000C diamine.

<table>
<thead>
<tr>
<th>Example 1 Construction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core diameter (in)</td>
</tr>
<tr>
<td>Core Specific Gravity</td>
</tr>
<tr>
<td>Core Compression (PGA)</td>
</tr>
<tr>
<td>Inner Cover Thickness (in)</td>
</tr>
<tr>
<td>Inner Cover Hardness (Shore D)</td>
</tr>
<tr>
<td>Outer Cover Composition</td>
</tr>
<tr>
<td>Outer Cover Thickness (in)</td>
</tr>
<tr>
<td>Outer Cover Hardness (Shore D)</td>
</tr>
<tr>
<td>Ball Pole Size (in)</td>
</tr>
<tr>
<td>Ball Equator Size (in)</td>
</tr>
</tbody>
</table>

TABLE 2

Sound Level and Frequency of Example 1 and Comparative Commercial Balls

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Ball</th>
<th>Construction*</th>
<th>Frequency (Hz)</th>
<th>Sound Pressure Level (dB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex 1</td>
<td>Ex 1</td>
<td>3 piece/solid core/Thermoset PU cover</td>
<td>3360</td>
<td>80.9</td>
</tr>
<tr>
<td>Comp Ex 1</td>
<td>Bridgestone TSX01</td>
<td>3 Piece/Solid core/TPU cover</td>
<td>3710</td>
<td>84.8</td>
</tr>
<tr>
<td>Comp Ex 2</td>
<td>Bridgestone TSX01h</td>
<td>3 Piece/Solid core/TPU cover</td>
<td>3980</td>
<td>85.1</td>
</tr>
<tr>
<td>Comp Ex 3</td>
<td>Bridgestone TSX01s</td>
<td>3 Piece/Solid core/TPU cover</td>
<td>3360</td>
<td>81.5</td>
</tr>
<tr>
<td>Comp Ex 4</td>
<td>Srixon Zara</td>
<td>3 Piece/Solid core/TPU cover</td>
<td>3760</td>
<td>84.0</td>
</tr>
<tr>
<td>Comp Ex 5</td>
<td>Srixon Zara</td>
<td>3 Piece/Solid core/TPU cover</td>
<td>3750</td>
<td>83.9</td>
</tr>
<tr>
<td>Comp Ex 6</td>
<td>Srixon Zara</td>
<td>3 Piece/Solid core/TPU cover</td>
<td>3400</td>
<td>81.8</td>
</tr>
<tr>
<td>Comp Ex 7</td>
<td>Bridgestone B330S</td>
<td>3 Piece/Solid core/TPU cover</td>
<td>3610</td>
<td>82.5</td>
</tr>
<tr>
<td>Comp Ex 8</td>
<td>Bridgestone E5</td>
<td>3 Piece/Solid core/TPU cover</td>
<td>3450</td>
<td>83.5</td>
</tr>
<tr>
<td>Comp Ex 9</td>
<td>Maxifi Elite</td>
<td>3 Piece/Wound core/Thermoset PU cover</td>
<td>3170</td>
<td>80.5</td>
</tr>
</tbody>
</table>
TABLE 2-continued

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Ball Construction*</th>
<th>Frequency (Hz)</th>
<th>Sound Pressure Level (dB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp Ex 10</td>
<td>Maxfli HT-Balata 3 Piece/Wound core/Thermoset PU cover</td>
<td>3000</td>
<td>79.0</td>
</tr>
<tr>
<td>Comp Ex 11</td>
<td>Callaway HX Tour 3 Piece/Solid core/Thermoset PU cover</td>
<td>4060</td>
<td>84.5</td>
</tr>
<tr>
<td>Comp Ex 12</td>
<td>Nike One Black 3 Piece/Solid core/TPU cover</td>
<td>3400</td>
<td>82.2</td>
</tr>
<tr>
<td>Comp Ex 13</td>
<td>Titleist Professional 3 Piece/Wound core/Thermoset PU cover</td>
<td>3360</td>
<td>79.7</td>
</tr>
<tr>
<td>Comp Ex 14</td>
<td>Maxfli Revolution 3 Piece/Wound core/Thermoset PU cover</td>
<td>3370</td>
<td>81.8</td>
</tr>
<tr>
<td>Comp Ex 15</td>
<td>Maxfli Revolution V1 2 Piece/Solid core/Thermoset PU cover</td>
<td>3910</td>
<td>83.6</td>
</tr>
<tr>
<td>Comp Ex 16</td>
<td>Titleist V1 3 Piece/Solid core/Thermoset PU cover</td>
<td>3380</td>
<td>81.1</td>
</tr>
<tr>
<td>Comp Ex 17</td>
<td>Nike One Plat. 4 Piece/Solid core/TPU cover</td>
<td>3410</td>
<td>81.4</td>
</tr>
<tr>
<td>Comp Ex 18</td>
<td>Titleist Pro V1x 4 Piece/Solid core/Thermoset PU cover</td>
<td>3600</td>
<td>82.8</td>
</tr>
<tr>
<td>Comp Ex 19</td>
<td>Callaway Tour 56 3 Piece/solid core/Thermoset PU cover</td>
<td>3680</td>
<td>81.4</td>
</tr>
<tr>
<td>Comp Ex 20</td>
<td>TaylorMadeTP Red 3 Piece/solid core/Thermoset PU cover</td>
<td>3680</td>
<td>82.1</td>
</tr>
<tr>
<td>Comp Ex 21</td>
<td>Bridgestone B330 3 Piece Solid core TPU cover</td>
<td>3820</td>
<td>83.5</td>
</tr>
<tr>
<td>Comp Ex 22</td>
<td>TaylorMadeTP Black 3 Piece/solid core/Thermoset PU cover</td>
<td>3820</td>
<td>83.5</td>
</tr>
<tr>
<td>Comp Ex 23</td>
<td>Spalding Plus Extra Distance 2 Piece/solid core/ionomer cover</td>
<td>4650</td>
<td>87.0</td>
</tr>
</tbody>
</table>

*TPU = Thermoplastic polyurethane

We claim:

1. A golf ball comprising a cover layer, a core, and one or more intermediate layers, and wherein the ball has:
   1) a solid core;
   2) a cover comprising polyurethane, polyurea or a combination thereof; and
   3) a Sound Pressure Level, S, of less than 81 dB.

2. The golf ball of claim 1 wherein S meets the following inequality:

   \[ S < 0.32143 \times F + 189.5 \]

   where F is the golf ball frequency in Hz.

3. The golf ball of claim 1 wherein S meets the following inequality:

   \[ S < 0.01F + 112 \]

   where F is the golf ball frequency in Hz.

4. The golf ball of claim 3 wherein the cover comprises a thermoset polyurethane.

5. The golf ball of claim 1 wherein the cover comprises a polyurethane made from a polypropylene glycol-terminated toluene diisocyanate prepolymer.

6. The golf ball of claim 1 wherein the cover comprises a polyurethane made from the reaction product of a polypropylene glycol-terminated toluene diisocyanate prepolymer with a diamine.

7. The golf ball of claim 1, wherein the golf ball has a S of less than 80.5 dB.

8. The golf ball of claim 1, wherein the cover does not include an ionomer.

9. The golf ball of claim 1, wherein the cover consists essentially of a polyurethane.

10. The golf ball of claim 1, wherein the core includes at least one nanocomposite or nanofiller, the intermediate layer includes a polyalkenamer, and the cover layer includes a polyurethane.

11. A golf ball comprising a cover layer, a core, and one or more intermediate layers, and wherein the ball has:
   1) a solid core;
   2) a polyurethane cover or polyurea cover; and
   3) a Sound Pressure Level, S, of less than 81.5 dB, wherein S meets the following inequality:

   \[ S < 0.32143 \times F + 189.5 \]

   where F is the golf ball frequency in Hz.

12. The golf ball of claim 11, wherein the polyurethane cover comprises a thermoset polyurethane.

13. The golf ball of claim 11, wherein the golf ball includes a polyurethane cover.

14. The golf ball of claim 12, wherein the cover comprises a polyurethane made from a polypropylene glycol-terminated toluene diisocyanate prepolymer.

15. The golf ball of claim 11, wherein the core includes at least one nanocomposite or nanofiller, the intermediate layer includes a polyalkenamer, and the cover is a polyurethane cover layer.

16. A golf ball comprising a cover layer, a core, and one or more intermediate layers, and wherein the ball has:
   1) a solid core;
   2) a polyurethane cover or polyurea cover; and
3) a Sound Pressure Level, S, of less than 81.5 dB, wherein S meets the following inequality:

\[ S < 0.01F + 112 \]

where F is the golf ball frequency in Hz.

17. The golf ball of claim 16, wherein the polyurethane cover comprises a thermoset polyurethane.

18. The golf ball of claim 16, wherein the golf ball includes a polyurethane cover.

19. The golf ball of claim 16, wherein the core includes at least one nanocomposite or nanofiller, the intermediate layer includes a polyalkenamer, and the cover is a polyurethane cover layer.

20. A golf ball comprising a cover layer, a core, and one or more intermediate layers, and wherein the ball has:
   1) a solid core; and
   2) a thermoset polyurethane cover;

   wherein the golf ball has a golf ball frequency of \( \leq 3360 \) Hz.

21. The golf ball of claim 20, wherein the golf ball has a golf ball frequency of \(< 3360 \) Hz.

22. The golf ball of claim 20, wherein the cover comprises a polyurethane made from a polypropylene glycol-terminated toluene diisocyanate prepolymer.

23. The golf ball of claim 20, wherein the core includes at least one nanocomposite or nanofiller, and the intermediate layer includes a polyalkenamer.

24. A golf ball comprising a cover layer, a core, and one or more intermediate layers, and wherein the ball has
   1) a solid core; and
   2) a polyurethane cover or polyurea cover;

   wherein the golf ball has a golf ball frequency of \(< 3360 \) Hz.

* * * * *