A golf ball having a core and cover, the cover including an outermost cover layer, is disclosed. The outermost cover layer is relatively thin and provides resistance to scratching and scuffing of the ball's cover layer, while maintaining desirable playability characteristics. The outermost cover layer is formed from a thermoplastic material, has a Shore D hardness of at least 56, and a Shore D hardness at least as hard as a layer disposed between the outermost layer and the core.
GOLF BALL HAVING VERY THIN OUTERMOST COVER LAYER FOR IMPROVED SCUFF RESISTANCE

FIELD OF THE INVENTION

This invention relates to a golf ball, and particularly, a multi-layer golf ball having a very thin outermost cover layer that improves resistance to scuffing and scratching of the ball.

BACKGROUND OF THE INVENTION

There has been a longstanding trade-off in golf ball technology between playability (a ball’s spin, click, feel, etc.) and durability (scuff, cut, marking, and abrasion resistance, fatigue endurance, etc.). Generally, a thicker and harder golf cover is more durable than a thinner and softer cover. A golf ball with a thick, hard cover gives the ball maximal durability and would be beneficial to the less experienced golfer. However, a thick, hard cover greatly sacrifices a golf ball’s playability, a quality experienced golfers desire. Thus, over the years, various types of golf balls have been developed in an attempt to resolve this dilemma.

Traditionally, golf balls have been categorized in three different groups: one-piece balls, multi-piece (two or more pieces) solid balls, and wound (three-piece) balls. The one-piece ball is typically formed from a solid mass of moldable material, which has been cured to develop the necessary degree of hardness. It possesses no significant difference in composition between the interior and exterior of the ball. These balls do not have an enclosing cover. One-piece balls are described, for example, in U.S. Pat. Nos. 3,513,545, 3,573,123, and 3,584,612.

The wound ball is frequently referred to as a three-piece ball since it is made with a vulcanized rubber thread wound under tension around a solid or semi-solid core and thereafter enclosed in a single or multi-layer covering of tough protective material. While for many years the wound ball satisfied the standards of both the U.S.G.A. and most golfers, it has several disadvantages. For example, a wound ball is difficult to manufacture due to the number of production steps required and the careful control, which must be exercised in each stage of manufacture to achieve suitable roundness, velocity, rebound, click, feel, and the like.

The three-piece wound ball typically has a balata cover, which is relatively soft and flexible. Upon impact, it compresses against the surface of the club producing high spin. Consequently, the soft and flexible balata covers provide an experienced golfer with the ability to apply a spin to control the ball in flight in order to produce a draw or a fade or a backs pin, which causes the ball to “bite” or stop abruptly on contact with the green. Moreover, the soft balata cover produces a soft “feel” to the low handicap player. Such playability properties of workability, feel, etc. are particularly important in short iron play with low swing speeds and are exploited significantly by relatively skilled players.

Despite all the benefits of balata covered balls, they are easily cut and/or damaged if hit incorrectly. Thus, golf balls produced with balata or balata containing cover compositions have a relatively short life span. As a result of this negative property, balata and its synthetic substitute, transpolyisoprene and resin blends, have been essentially replaced as the cover materials of choice by new cover materials comprising ionomeric resins.

One important development in balancing the playability-durability dilemma found in one-piece and wound play has been the multi-layered golf ball. Generally, multi-layered golf balls have cores designed for “driver distance”, mid-layers designed for full iron shots, and covers designed for maximal “feel” and spin in half-shots, chips, and puts.

U.S. Pat. Nos. 4,431,193 and 4,919,434 disclose multi-layer golf balls. Multi-layered golf balls attempt to achieve playability with a “soft”-type solid or liquid core, while the multiple layers of the molded covers attempt to maximize the protection of the ball from cutting and scuffing. Solid cores are generally made of polybutadiene, while molded covers are generally made from natural balata, synthetic balata, or ionomeric resins.

Ionomeric resins are polymers containing interchain ionic bonding. Ionomeric resins are known to have superior toughness, durability, and flight characteristics, and as a result of these characteristics, various ionomeric resins sold by E. I. DuPont de Nemours & Company under trademark “Surlyn®” and by the Exxon Corporation (see U.S. Pat. No. 4,911,451) under trademarks “Excor®” and the trade name “Iotek”, have become the materials of choice for the construction of golf ball covers over the traditional “balata” (transpolyisoprene, natural or synthetic) rubbers. The softer balata covers, although exhibiting enhanced playability properties, lack the durability (cut and abrasion resistance, fatigue endurance, etc.) properties that ionomer resins possess which are required for repetitive play or for use by less experienced golfers.

Ionomeric resins are generally ionic copolymers of an olefin, such as ethylene, and a metal salt of an unsaturated carboxylic acid, such as acrylic acid, methacrylic acid, or maleic acid. Metal ions, such as sodium or zinc, are used to neutralize some portion of the acidic group in the copolymer resulting in a thermoplastic elastomer exhibiting enhanced properties, i.e., durability, etc., for golf ball cover construction over balata.

Currently, more than fifty (50) commercial grades of ionomers are available both from Exxon and DuPont, with a wide range of properties which vary according to the type and amount of metal cations, molecular weight, composition of the base resin (i.e., relative content of ethylene and methacrylic and/or acrylic acid groups) and additive ingredients, such as reinforcement agents. A great deal of research continues in developing ionomeric materials for golf balls exhibiting the desired combination of the properties of both playability and durability.

Various non-ionomeric thermoplastic materials have been used for golf ball covers in order to increase playability, but have been found inferior to ionomers in achieving good cut resistance and travel distance. It would be useful to obtain a golf ball having a cover which incorporates non-ionomeric materials creating favorable playability characteristics, while achieving favorable durability characteristics of a ball having a cover which primarily contains ionomers.

Recently, several patents have been issued which attempt to achieve favorable playability and durability char-
characteristics. For example, U.S. Pat. No. 4,431,193 discloses a multi-layer ball with a hard ionomer inner cover layer and a soft outer cover layer. U.S. Pat. No. 4,919,434 discloses a golf ball with a 0.4-2.2 mm thick cover made from two thermoplastic cover layers.

[0014] U.S. Pat. No. 5,628,699 discloses a wound golf ball with an inner layer having a higher Shore D hardness than the outer layer. The outer layer has a thickness of 0.4 to 3.3 mm and has a Shore D hardness of 40 to 55. The inner layer is formed of a different ionomer resin from the outer layer and has a Shore D hardness of 55 to 68.

[0015] U.S. Pat. No. 5,674,137 discloses a wound golf ball with a cover having a multi-layered structure having a total thickness of 1.0 to 4.0 mm. The outer layer has a thickness of 0.4 to 3.0 mm and a particular first hardness. The inner layer has a second hardness higher than the first hardness. The outer layer is formed of a first ionomer or balata rubber resin having a Shore D hardness of 40 to 55, and the inner layer is formed of a second ionomer or balata rubber resin having a Shore D hardness of 55 to 68. The difference in hardness between the first and second resins is at least 5 in Shore D hardness.

[0016] U.S. Pat. No. 5,779,562 discloses a multi-core, multi-cover golf ball. The cover includes an inner cover layer and an outer cover layer enclosing the inner cover layer. The outer cover layer has a Shore D hardness of no more than 55, and the outer cover layer has a Shore D hardness less than the inner cover layer 15 layer.

[0017] U.S. Pat. No. 5,803,831 discloses a multi-layered golf ball having a soft outer cover. The golf ball has a thermoplastic inner cover layer with a preferable Shore D hardness of at least 65, and an outer cover layer with a Shore D hardness of 55 or less.

[0018] Unfortunately, the durability of the multi-layered golf balls described above suffer with a softer outer layer which increases the likelihood of scuffing, cutting, and scratching. Each of the above noted patents disclose an outer layer having a Shore D hardness no greater than 55. Also, the above noted patents also disclose that the Shore D hardness of the outer layer is less than the inner cover layer. The durability of such golf balls would suffer as less experienced golfers are more prone to scuffs, cuts, and scratches. Therefore, it would be advantageous to have a golf ball with the playability of the golf balls described in the above noted patents while having improved durability, namely scuff, cutting, and scratching resistance.

SUMMARY OF THE INVENTION

[0019] The present invention is directed toward a golf ball with a very thin outermost cover layer that provides the ball durability characteristics such as scuff, cutting, and scratch resistance while maintaining desirable playability characteristics when struck with golf clubs.

[0020] The present invention is further directed toward a golf ball which comprises a core and a cover including a very thin outermost cover layer, wherein the outermost cover layer comprises a thermoplastic material, has a thickness of less than about 0.040 inches, a Shore D hardness of at least 56, and a Shore D hardness at least as hard as a layer between the outermost layer and core.

[0021] In another aspect, the present invention is further directed toward a golf ball which comprises a core and a cover including a very thin outermost cover layer disposed about an inner cover layer, wherein the outermost cover layer comprises a thermoplastic material, has a thickness of less than about 0.040 inches, a Shore D hardness of at least 56, and a Shore D hardness at least as hard as the layer below it.

[0022] In yet another aspect, the present invention provides a golf ball comprising a core, at least one mantle layer including a woven elastomer thread, and a cover including a very thin outermost cover layer, wherein the outermost cover layer comprises a thermoplastic material, has a thickness of less than about 0.040 inches, a Shore D hardness of at least 56, and a Shore D hardness at least as hard as the layer below it.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] FIG. 1 is a partial sectional view of a preferred embodiment golf ball in accordance with the present invention;

[0024] FIG. 2 is a partial sectional view of another preferred embodiment golf ball in accordance with the present invention;

[0025] FIG. 3 is a partial sectional view of another preferred embodiment golf ball in accordance with the present invention; and

[0026] FIG. 4 is a partial sectional view of yet another preferred embodiment golf ball in accordance with the present invention.

[0027] It will be appreciated that these drawings are not necessarily to scale and are schematic in nature.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0028] The present invention provides a golf ball, and preferably a multi-layer golf ball, comprising a very thin outermost cover layer that imparts improved scuff or scratch resistance properties to the ball.

[0029] As described in greater detail herein, in a preferred embodiment, the present invention golf ball comprises a core, optional mantle layer, optional wound layer and/or wound core layer, a cover or cover layer, and an outermost protective layer. In a particularly preferred embodiment, a multi-layer cover assembly is used for the cover of the present invention golf ball, wherein the outer cover layer of that assembly is formed and provided as described herein, and serves as the outer protective layer. In another particularly preferred embodiment, a multi-layer cover assembly is formed and provided as described herein, and upon which is disposed, an outer protective layer as described herein. The present invention also includes golf ball embodiments utilizing outermost protective layers formed or otherwise disposed upon single cover layers and cover layer assemblies of three or more cover layers.

[0030] Referring to FIG. 1, the present invention is particularly directed toward a multi-layer golf ball 1 which comprises a core 2, at least one cover layer 3 comprising an outermost cover layer and at least one mantle layer 4 disposed therebetween.
[0031] In another preferred embodiment of the present invention, illustrated in FIG. 2, a golf ball 10 is shown having an inner cover layer 16 and an outer cover layer 18 which comprises an outermost cover layer, disposed about a mantle 14 and core 12.

[0032] In another preferred embodiment, the present invention provides a golf ball comprising a wound interior layer, such as shown in FIGS. 3 and 4. Specifically, FIG. 3 illustrates a preferred embodiment golf ball 20 comprising a core 22, a wound layer 24 disposed about and immediately adjacent to the core 22, a mantle layer 26, and a cover 28 comprising an outermost cover layer. The cover 28 may include an inner and outer cover layer as previously described with regard to the preferred embodiment golf ball 10 depicted in FIG. 2.

[0033] FIG. 4 illustrates yet another preferred embodiment golf ball 30 comprising a core 32, a mantle layer 34 disposed about and immediately adjacent to the core 32, a wound layer 36 disposed about the mantle and core, and a cover 38. The cover 38 may include inner and outer cover layers as previously described with regard to the preferred embodiment golf ball 10.

[0034] Before addressing the characteristics and features of the preferred embodiment scuff resistant outermost layer, it is instructive to address the other components of the preferred embodiment golf balls in accordance with the present invention.

Core

[0035] The core of the present invention golf ball may comprise a variety of materials, including those conventionally employed as golf ball cores. Typical materials for such cores include core compositions having a base rubber, a crosslinking agent, a filler, and a co-crosslinking agent. The base rubber typically includes natural or synthetic rubbers. A preferred base rubber is 1,4-polybutadiene having a cis-structure of at least 40%. Natural rubber, polyisoprene rubber and/or styrene-butadiene rubber may be optionally added to the 1,4-polybutadiene. The initiator included in the core composition can be any known polymerization initiator which decomposes during the cure cycle. The crosslinking agent includes a metal salt such as a zinc salt or a magnesium salt from an unsaturated fatty acid having 3 to 8 carbon atoms such as acrylic or methacrylic acid. The filler typically includes materials such as zinc oxide, barium sulfate, silica, calcium carbonate, zinc carbonate, and the like.

[0036] In a preferred aspect, the core is a cross-linked 1,4-polybutadiene having a specific gravity greater than 1.2, and, more preferably, about 1.25. The high specific gravity of the core decreases the spin rate of the ball for a lower flight path. Also, the PGA compression of the core is preferably greater than 60, and more preferably, about 65.

[0037] In another preferred aspect, the core of the golf ball is made of a crosslinked unsaturated elastomer and preferably comprises a thermoset rubber such as polybutadiene, but can also be made of other core materials which would provide a sufficient coefficient of restitution (COR). The core imparts upon the finished golf ball a COR of at least 0.780, and preferably at least 0.790.

[0038] The diameter of the core is determined based upon the desired overall ball diameter, minus the combined thickness of the inner and outer cover layers. The core typically has a diameter of about 1.0-1.6 inches, preferably 1.4-1.6 inches, a PGA compression of 80-100, and a COR in the range of 0.770-0.830.

[0039] Conventional solid cores are typically compression molded from a slug of uncured or lightly cured elastomer composition comprising a high cis content polybutadiene, and a metal salt of an α, β ethylenically unsaturated carboxylic acid such as zinc mono- or di-acrylate or meth-acrylate. To achieve a higher COR in the core, the manufacturer may include a filler such as small amounts of a metal oxide, e.g., zinc oxide. In addition, larger amounts of metal oxide other than those that are needed to achieve the desired COR are often included in conventional cores in order to increase the core weight so that the finished ball more closely approaches the U.S.G.A. upper weight limit of 1.620 ounces.

[0040] Other materials may be used in the core composition including compatible rubbers or ionomers, and low molecular weight fatty acids such as stearic acid. Free radical initiators such as peroxides are admixed with the core composition so that on the application of heat and pressure, a complex curing cross-linking reaction takes place. The core, such as core 2 in FIG. 1, core 12 in FIG. 2, core 22 in FIG. 3, and core 32 in FIG. 4, may be composed of any one or more of the materials herein described.

[0041] In one embodiment of the present invention, the core comprises a center which is liquid-filled or solid around which an elastic thread is wound such as core 22 in FIG. 3, and core 32 in FIG. 4. The solid center is typically a homogenous mass of a resilient material such as polybutadiene or a natural rubber. The liquid-filled center is typically a thin-walled sphere into which a liquid such as corn syrup is injected by means of a hypodermic needle. The sphere is then sealed and frozen to make the center a solid mass. The windings for either type of center are provided by an elastic thread, which is stretched and wound about the center to a desired thickness.

[0042] Conventionally, the centers of wound cores have a diameter of about 1.000 to about 1.125 inches. Typically, the outer diameter of a conventional wound core is about 92% of the overall diameter of the finished ball. However, the outer diameter of wound cores employed in this embodiment of the present invention have an overall diameter of less than 90% of the overall diameter of the finished ball. Preferably, the wound cores have a diameter of about 75-90% of the overall diameter of the finished ball. Most preferably, the wound cores of the present invention have an overall diameter of about 85% of the overall diameter of the finished ball.

[0043] In another embodiment, the core may comprise more than one layer, i.e., the core may be multi-layered. At least one layer is disposed about the core. Also, the multi-layered core may optionally be wound with an elastic thread.

[0044] An extensive discussion of suitable materials and processes for forming golf ball cores for use in the present invention is found in U.S. Pat. Nos. 5,833,553; 5,830,087; 5,827,167; 5,820,489; 5,820,488; 5,803,831; 5,779,562; and 5,480,155, all of which are hereby incorporated by reference.
Optional Mantle Layer(s)

[0045] The mantle layer such as layer 4 in FIG. 1, layer 14 in FIG. 2, layer 26 in FIG. 3, and layer 34 in FIG. 4, comprises a wide array of materials such as thermoplastic polyester, thermoplastic polyetherester, dynamically vulcanized thermoplastic elastomer, functionalized styrene-butadiene elastomer, thermoplastic polyurethane or metalloocene polymer, or blends thereof.

[0046] In a preferred embodiment of the present invention, the mantle layer is a thermoplastic polyetherester. Suitable thermoplastic polyetheresters include Hytrek® 3078, Hytrek® G3548W, and Hytrek® G4078W, which are commercially available from DuPont. Hytrek® 3078 is the most preferred. The mantle layer preferably has a specific gravity greater than 1 and less than 1.2.

[0047] Suitable dynamically vulcanized thermoplastic elastomers include Santoprene®, Sarlink®, Vyram®, Dytron®, and Vistaflex®. Santoprene® is the trademark for a dynamically vulcanized PP/EPRDM. Santoprene® 203-40 is an example of a preferred Santoprene® and is commercially available from Advanced Elastomer Systems.

[0048] Examples of suitable functionalized styrene-butadiene elastomers include Kraton® FG-1901x and FG-1921x, which are available from the Shell Corporation.

[0049] Examples of suitable thermoplastic polyurethane include Estane® 58133, Estane® 58134, and Estane® 58144, which are commercially available from the B. F. Goodrich Company.

[0050] Suitable metalloocene polymers whose melting points are higher than the cover materials can also be employed in the mantle layer of the present invention.

[0051] Further, the materials for the mantle layer described above may be in the form of a foamed polymeric material. For example, suitable metallocone polymers include foams of thermoplastic elastomers based on metallocone single-site catalyst-based foams. Such metallocone-based foam resins are commercially available from Sentinel Products located in Hyannis, Mass.

[0052] The mantle layer may comprise up to 100% by weight a dynamically vulcanized thermoplastic elastomer, a functionalized styrene-butadiene elastomer, a thermoplastic polyurethane, a metallocone polymer, or blends thereof. In a preferred embodiment of the present invention, the mantle layer comprises Santoprene®, thermoplastic polyurethane, or blends thereof.

[0053] In another preferred embodiment of the present invention, the mantle layer is a blend of a first and a second thermoplastic polymer, wherein the first thermoplastic polymer is a dynamically vulcanized thermoplastic elastomer, a functionalized styrene-butadiene elastomer, a thermoplastic polyurethane or a metallocone polymer, and the second thermoplastic is a material such as a thermoplastic polyeurthane, a thermoplastic polyetherester or polyetheramide, a thermoplastic ionomer resin, a thermoplastic polyester, another dynamically vulcanized elastomer, another functionalized styrene-butadiene elastomer, another metallocone polymer, or blends thereof.

[0054] Suitable thermoplastic polyetheresters for use in this blended embodiment include Hytrek® 3078, Hytrek® G3548W, and Hytrek® G4078W, which are commercially available from DuPont. Suitable thermoplastic polyethers and thermoplastic ionomers include Pebax® 2533, Pebax® 3533, and Pebax® 4033, which are available fromElf-Atochem. Suitable thermoplastic ionomers resins include any number of olefinic based ionomers including SURLYN® and Iotek®), which are commercially available from DuPont and Exxon, respectively. The flexural moduli for these ionomers is about 100 kpsi to about 200 kpsi. Suitable thermoplastic polyesters include polybutylene terephthalate. Likewise, the dynamically vulcanized thermoplastic elastomers, functionalized styrene-butadiene elastomers, thermoplastic polyurethane, or metallocone polymers identified above are also useful as the second thermoplastic in such blends. Further, the materials of the second thermoplastic described above may be in the form of a foamed polymeric material.

[0055] Such thermoplastic blends comprise about 1% to about 99% by weight of a first thermoplastic material, and about 99% to about 1% by weight of a second thermoplastic material. Preferably, the thermoplastic blend comprises about 5% to about 95% by weight of a first thermoplastic material, and about 5% to about 95% by weight of a second thermoplastic material. In a preferred embodiment of the present invention, the first thermoplastic material of the blend is a dynamically vulcanized thermoplastic elastomer, such as Santoprene®.

[0056] Alternative embodiments of the present invention golf ball include a ball with more than one mantle layer. If more than one mantle layer is used, the mantle layers do not have to be in contact with one another, i.e., the mantle layers may be disposed between various layers of the golf ball without touching one another.

[0057] Other suitable materials and descriptions for forming mantles in the present invention golf balls are found in U.S. Pat. Nos. 5,833,554; 5,779,562; 5,733,206; and 5,480,155, all of which are hereby incorporated by reference.

Cover

[0058] The cover layer of the present invention golf balls comprises at least one layer of a thermoplastic or thermo-setting material. The cover layer is shown in FIG. 1 as layer 3, in FIG. 2, as layers 16 and 18, in FIG. 3 as layer 28, and in FIG. 4 as layer 38. Any number of a wide variety of cover materials may be used in the present invention golf balls. Among the preferred conventional cover materials are ionomer resins and low modulus ionomers obtained by providing a cross metallic bond to polymers of monooleinins with at least one member selected from the group consisting of unsaturated mono- or di-carboxylic acids having 3 to 12 carbon atoms and esters thereof. The polymers contain 1 to 50% by weight of the unsaturated mono- or di-carboxylic acid and/or ester thereof. More particularly, low modulus ionomers, such as acid-containing ethylene copolymer ionomers, include E/XY copolymers. E is ethylene. X is a softening comonomer such as acrylate or methacrylate present in 0-50, preferably 0-25, and most preferably 0-2, weight percent of the polymer. Y is acrylic or methacrylic acid present in 5-35, preferably 10-35, and most preferably 15-20, weight percent of the polymer, wherein the acid moiety is neutralized 1-90%, preferably at least 40%, and most preferably at least about 60%, to form an ionomer by a cation. Examples of suitable cations include lithium,
sodium, potassium, magnesium, calcium, barium, lead, tin, zinc or aluminum, or a combination of such cations. Preferred cations include lithium, sodium, magnesium, and zinc. Specific acid-containing ethylene copolymers include ethylene/acrylic acid, ethylene/methacrylic acid, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/n-butyl acrylate, ethylene/methacrylic acid/iso-butyl acrylate, ethylene/methacrylic acid/n-butyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacrylate. Preferred acid-containing ethylene copolymers include ethylene/methacrylic acid, ethylene/acrylic acid, ethylene/methacrylic acid/n-butyl acrylate, ethylene/acrylic acid/n-butyl methacrylate, ethylene/acrylic acid/n-butyl acrylate copolymers. The most preferred acid-containing ethylene copolymers are ethylene/methacrylic acid, ethylene/acrylic acid, ethylene/methacrylic acid/n-butyl acrylate, ethylene/methacrylic acid/ethyl acrylate, and ethylenel-(meth) acrylic acid/methyl acrylate copolymers.

[0059] The manner in which these ionomers are made is well known in the art as described in, e.g., U.S. Pat. No. 3,264,272, hereby incorporated by reference. Such ionomer resins are commercially available from DuPont Co. under the tradename SURLYN®. The presently preferred cover material is a 50/50 blend of SURLYN® 8140 and SURLYN® 7940, which are high acid sodium and standard lithium SURLYN®, respectively. This cover material has a flex modulus of about 85 kpsi and a specific gravity of about 0.95. Another preferred cover is comprised of a 50/50 blend of SURLYN® 8140 and SURLYN® SEP671, which is a lithium SURLYN® having about 19% methacrylic acid. This material has a flex modulus of about 105 kpsi. Preferably, the flex modulus of the cover is greater than 80 kpsi. Still further, the preferred cover has a hardness of about 70 Shore D. The high flex modulus of the cover provides increased initial velocity and a low spin rate.

[0060] In a preferred aspect, a multi-layer cover is utilized, such as shown in FIG. 2. Preferably, the inner layer 16 of the cover is either a thermoplastic material such as a thermoplastic elastomer, a thermoplastic rubber, a thermoset rubber, or a thermoset elastomer material. Additional examples of materials suitable for use as the inner cover layer include polyether or polyester thermoplastic urethanes as well as thermoset polyurethanes. A preferable thermoplastic material is a thermoplastic urethane with a melting point of about 178° to about 205° F. A preferable thermoset material is a rubber-based, castable urethane. Preferably, the outer layer 18 of the cover is either a thermoplastic plastic material such as an elastomer or a thermoplastic rubber, or a thermosetting material. Suitable materials are for the outer layer include urethanes, ionomers with a low modulus and other “dead” but durable materials such as EPDM and butyl rubber. Additionally, the present invention also contemplates the use of a polymeric foam material, such as the metalloocene-based foamed resin described above, as the material for either the outer cover layer or the inner cover layer, but preferably not both layers.

[0061] In one embodiment of the present invention, it is preferable that the thermoplastic or thermosetting materials of the outer layer have a melting point or heat of reaction (cure) temperature less than the melting point or heat of reaction (cure) temperature of the materials of the inner layer.

[0062] The inner and outer cover layers of this embodiment of the invention can be molded about the core and mantle layers through a variety of conventional molding methods. For example, the cover layers can be compression molded, retractive pin injection molded, fixed pin injection molded, cast around the core and mantle or a combination thereof. However, it is important that the materials of the outer layer are characterized in that they have thermal properties such that no flow of the inner layer material occurs during the molding of the outer cover layer about the inner layer, regardless of the process employed to mold the layers.

[0063] The present invention also contemplates the use of a variety of non-conventional cover materials. In particular, the covers of the present invention golf balls may comprise thermoplastic or engineering plastics such as ethylene or propylene based homopolymers and copolymers including functional monomers such as acrylic and methacrylic acid and fully or partially neutralized ionomers and their blends, methyl acrylate, methyl methacrylate homopolymers and copolymers, imidized, amino group containing polymers, polycarbonate, reinforced polyamides, polyphenylene oxide, high impact polystyrene, polyether ketone, polysulfone, poly(phenylene sulfide), reinforced engineering plastics, acrylonitrile-butadiene, acrylonitrile-acrylonitrile, poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene-vinyl alcohol), poly(tetrafluoroethylene) and their copolymers including functional comonomers and blends thereof. These polymers or copolymers can be further reinforced by blending with a wide range of fillers and glass fibers, spheres, or wood pulp.

[0064] In a preferred form of the invention, the inner cover layer comprises an ionomer with an average weight percent (wt %) acid content of about 15 or less which is at least 10% neutralized. In a particularly preferred form of the invention, the inner cover layer, such as layer 16 shown in FIG. 2 constitutes a blend of two types of ionomers in which one component of the blend is an ethylene-acrylic acid or ethylene-methacrylic acid copolymer containing at least 15 wt % acid groups which are at least partially neutralized with a cation, and the other type of ionomer is a terpolymer of ethylene, acrylic acid or methacrylic acid and a softening termonomer such as butyl acrylate or methyl acrylate, resulting in an overall wt % acid content of about 15 or less.

[0065] The outer cover layer may also comprise an ionomer. The outer layer, such as layer 18 in FIG. 2, can contain a single type of ionomer or a blend of two or more types of ionomers. Furthermore, a hardening and/or softening modifier can be added. The outer cover layer is harder than the inner cover layer, and has a Shore D hardness of about 60 or more, more preferably 65 or more and most preferably 68 or more (ASTM D-2240). In a particularly preferred form of the invention, the outer cover layer contains an ionomer having at least 16 weight % acid groups, which are at least partially neutralized.

[0066] As described in greater detail herein, for golf ball embodiments in which an outmost cover layer is formed or otherwise disposed on a multi-layer cover assembly, and thus, the outer cover layer of the cover assembly is not
designed to serve as this protective layer, the thicknesses for the inner and outer cover layers are as follows. The inner and outer layers together form a cover having a thickness of about 0.100 to about 0.250 inches, more preferably about 0.10 to about 0.20 inches, and most preferably about 0.11 to about 0.15 inches. Preferably, the inner cover layer has a thickness of about 0.025 to about 0.200 inches, and more preferably from about 0.050 to about 0.100 inches. The outer cover layer preferably has a thickness of about 0.025 to 0.200 inches, or more preferably from about 0.050 to about 0.100 inches. The ratio of the diameter of the ball to the thickness of the cover, i.e., the sum of the thickness of the inner cover layer and the outer cover layer, is no more than about 17:1, and more preferably no more than about 15:1.

[0067] The hardness of the inner and outer cover layers, and the compositions and thicknesses of these layers are appropriate to result in a golf ball having a COR of at least 0.780, more preferably at least 0.790 and most preferably at least 0.800. The golf ball of the invention has an overall PGA compression of from about 30 to about 110, more preferably from about 50 to about 107, and most preferably from about 60 to about 90.

[0068] Preferably, the spin rate of the golf balls is no more than about 8000 revolutions per minute (rpm) when struck with a 9-iron under the conditions of launch angle, ball speed and tee position which produce a spin rate of about 7100 rpm for a two-piece hard covered ball (1994 Top-Flite XL) and a spin rate of about 9700 rpm for a thread wound balata covered ball (1994 Titleist Tour 100) using the same club. This relatively low spin rate provides the advantage of less sideways spin for improved accuracy and less backspin for improved rolling distance.

[0069] More particularly, the inner cover layer preferably comprises an ionomer having an average wt % acid content of about 15 or less which is at least 10% neutralized. Preferably, the inner cover layer such as layer 16 in FIG. 2, includes a blend of hard and soft ionomer resins including but not limited to those described in U.S. Pat. Nos. 4,884, 814 and 5,120,791, both of which are incorporated herein by reference. For example, a blend of a high modulus ionomer (i.e., a hard ionomer) and a low modulus ionomer (i.e., a soft ionomer) in a mixture can be used. A high modulus ionomer is one which has a flexural modulus of about 15,000-70,000 psi or more as measured under ASTM method D-790. The hardness of this type of ionomer is at least 50 on the Shore D scale as measured in accordance with ASTM method D-2240. A low modulus ionomer which can be blended with the high modulus ionomer to form an inner layer, should have a flexural modulus of about 1,000 to about 15,000 psi (ASTM D-790), and a hardness of about 20 to about 40 on the Shore D scale (ASTM D-2240).

[0070] The hard ionomer resins used in blends to form the inner cover layer include ionomer copolymers which are the, e.g., sodium, zinc, magnesium, calcium, manganese, nickel, potassium or lithium, etc., salt, or blend thereof, of the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monoaacryl acid having from 3 to 8 carbon atoms and which result in a ball having the desired combination of COR, compression, and inner cover layer hardness. The carboxylic acid groups of the copolymer may be totally or partially, that is from about 10 to about 100%, neutralized. The hard ionomeric resins typically are copolymers of ethylene with acrylonitrile and/or methylacrylic acid. Two or more hard ionomer resins can be blended.

[0071] The metal cation salts utilized in the invention are preferably those salts which provide the metal cations capable of neutralizing, to various extents, the carboxylic acid groups of the high acid copolymer. These include acetate, oxide or hydroxide salts of, e.g., lithium, calcium, zinc, sodium, potassium, nickel, magnesium, and manganese, etc.

[0072] Examples of such lithium ion sources are lithium hydroxide monohydrate, lithium hydroxide, lithium oxide and lithium acetate. Sources for the calcium ion include calcium hydroxide, calcium acetate and calcium oxide. Suitable zinc ion sources are zinc acetate dihydrate and zinc acetate, a blend of zinc oxide and acetic acid. Examples of sodium ion sources are sodium hydroxide and sodium acetate. Sources for the potassium ion include potassium hydroxide and potassium acetate. Suitable nickel ion sources are nickel acetate, nickel oxide and nickel hydroxide. Sources of magnesium include magnesium oxide, magnesium hydroxide and magnesium acetate. Sources of manganese include manganese acetate and manganese oxide.

[0073] The metal cation neutralized high acid ionomer resins can be produced by reacting the high acid base copolymer with various amounts of the metal cation salts above the crystalline melting point of the copolymer, such as at a temperature from about 200° F to about 500° F, preferably from about 250° F to about 350° F; under high shear conditions at a pressure of from about 10 psi to 10,000 psi. Other blending techniques may also be used. The amount of metal cation salt utilized to produce the new metal cation neutralized high acid based ionomer resins is the quantity which provides a sufficient amount of the metal cations to neutralize the desired percentage of the carboxylic acid groups in the high acid copolymer. The extent of neutralization is generally from about 10% to about 90%.

[0074] Examples of commercially available hard ionomer resins which can be used in a blend to form the inner cover layer include the hard sodium ionomer copolymer sold under the trademark SURLYN® 8940 and the hard zinc ionomer copolymer sold under the trademark SURLYN® 9910. SURLYN® 8940 is a copolymer of ethylene with methacrylic acid with about 15 weight % acid which is about 29% neutralized with sodium ions. This resin has an average melt flow index of about 2.8. SURLYN® 9910 is a copolymer of ethylene and methacrylic acid with about 15 weight % acid which is about 58% neutralized with zinc ions. The average melt flow index of SURLYN® 9910 is about 0.7. Additional examples include Iotek 4000, Iotek 4010, Iotek 8000, Iotek 8020, Iotek 8030, Iotek 7010 and Iotek 7030 which are sold by Exxon Corporation. It is to be understood that the above examples are for illustrative purposes and are by no means intended to be limiting.

[0075] Non-limiting examples of soft ionomers to be blended with the above-described hard ionomers to form the inner cover layer of the inventive golf ball comprise sodium, zinc magnesium, calcium, manganese, nickel, potassium or lithium, etc., salts of a terpolymer of an olefin having from about 2 to 8 carbon atoms, acrylic acid or methacrylic acid, and a softening comonomer which is an unsaturated mono-mer of the acrylate ester class having from 1 to 21 carbon
atoms. The soft ionomer is preferably an ionomer made from an acrylic acid-based polymer and an unsaturated monomer of the acrylic ester class. The soft (low modulus) ionomers have a hardness from about 20 to 40 as measured on the Shore D scale and a flexural modulus from about 1,000 to about 15,000, as measured in accordance with ASTM method D-790.

[0076] Certain ethylene-acrylic acid-based soft ionomer resins developed by be Exxon Corporation under the designation “Iotek 7510” may be combined with known hard ionomers such as those indicated above to produce the inner cover. The combination produces higher CORs at equal or lower levels of hardness, higher melt flow (which corresponds to improved, more efficient molding, i.e., fewer rejects) as well as significant cost savings versus the outer layer of multi-layer balls produced by other known hard-soft ionomer blends as a result of the lower overall raw materials costs and improved yields. Furthermore, Iotek 75520, SURLYN® 8320 and SURLYN® 8120 also can be used.

[0077] It has been determined that when hard-soft ionomer blends are used for the inner cover layer, good results are achieved when the relative combination is in a range of about 90 to about 10% hard ionomer and about 10 to about 90% soft ionomer. The resins are improved by adjusting the ratio to about 75 to 25% hard ionomer and 25 to 75% soft ionomer. Even better results are noted at relative ranges of about 60 to 40% hard ionomer resin and about 40 to 60% soft ionomer resin.

[0078] Specific formulations which may be used in the cover composition are included in the examples set forth in U.S. Pat. Nos. 5,120,791 and 4,884,814, both patents of which are herein incorporated by reference. The present invention is in no way limited to those examples.

[0079] The outer cover layer such as layer 18 shown in FIG. 2 of the golf ball is harder than the inner cover layer, such as inner cover layer 16 of FIG. 2, and generally, but not necessarily, has a different chemical composition than the inner cover layer. The outer cover layer preferably comprises a high acid ionomer resin or high acid ionomer blend in which more than 10 weight % of the acid groups are neutralized. Preferably, the outer cover layer is formed from a blend of two or more high acid ionomer resins that are neutralized to different extents using different metal cations. Softening modifiers can be used to achieve the desired Shore D hardness of the outer cover layer.

[0080] The preferred high acid ionomers which can be used in formulating the outer cover layer of the golf ball are iodic polymers which are the metal salts of the reaction product of an olefin having from about 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from about 3 to 8 carbon atoms. As nonlimiting examples, sodium, zinc, magnesium, manganese, potassium, calcium, nickel and lithium can be used as the neutralizing cation. Preferably, the ionomeric resins are copolymers of ethylene with either acrylic or methacrylic acid. In some circumstances, an additional comonomer such as an acrylic ester, e.g., iso-n-butylacrylate, etc. can also be used to produce a somewhat softer terpolymer. The carboxylic acid groups of the copolymer are partially neutralized by the metal ions, i.e., from about 10 to about 75% or more preferably from about 30 to about 70%. Each of the high acid ionomer resins which may be included in the outer cover layer composition preferably contains more than 16% by weight of a carboxylic acid, preferably 17 to about 25% by weight of a carboxylic acid, and most preferably from about 18.5 to about 21.5% by weight of a carboxylic acid. Examples of commercially available high acid methacrylic acid-based ionomers which can be used in accordance with the invention include SURLYN® AD-8422 (sodium cation), SURLYN® 8162 (zinc cation), SURLYN® SEP-513-1 (zinc cation), and SURLYN® SEP-503-2 (magnesium cation). According to DuPont, all of these ionomers contain from about 18.5 to about 21% by weight methacrylic acid.

[0081] Examples of high acid acrylic acid-based ionomers which can be used in the present invention also include the Escor® or Iotek High Acid Ethylene Ionomers produced by Exxon, including Iotek EX-959 and Iotek EX-960. Furthermore, a number of other high acid ionomers neutralized to various extents by different types of metal cations, including manganese, lithium, potassium, calcium and nickel and several new high acid ionomers and/or high acid ionomer blends other than sodium, zinc and magnesium are now available for golf ball cover production.

[0082] As indicated above, softening comonomers can be included in the ionomeric inner and/or outer cover layers. Non-limiting examples of a softening comonomer include vinyl esters of aliphatic carboxylic acids wherein the acids have 2 to 10 carbon atoms, vinyl ethers wherein the alkyl group contains 1 to 10 carbon atoms, and alkyl acrylates or methacrylates wherein the alkyl group contains 1 to 10 carbon atoms. Suitable softening comonomers include vinyl acetate, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, or the like.

[0083] Examples of a number of copolymers suitable for use to produce the high acid ionomers used in the present invention include, but are not limited to, high acid embodiments of an ethylene/acrylic acid copolymer, an ethylene/methacrylic acid copolymer, an ethylene/itaconic acid copolymer, an ethylene/maleic acid copolymer, an ethylene/methacrylic acid/vinyl acetate copolymer, an ethylene/acrylic acid/vinyl alcohol copolymer, an ethylene/acrylic acid/vinyl alcohol copolymer, etc. The base copolymer broadly contains greater than 16% by weight unsaturated carboxylic acid, from about 30 to about 85% by weight ethylene and from 0 to about 40% by weight of a softening comonomer. Preferably, the copolymer contains about 20% by weight unsaturated carboxylic acid and about 80% by weight ethylene. Most preferably, the copolymer contains about 20% acrylic acid with the remaining being ethylene.

[0084] As indicated above, the inner cover layer and/or outer cover layer optionally may include hardening or softening modifiers, non-limiting examples of which include a metal stearate, such as zinc stearate, or another fatty acid salt, as described in commonly assigned U.S. Pat. Nos. 5,306,760 and 5,312,857, both of which are herein incorporated by reference. One purpose of the metal stearate or other fatty acid salt is to reduce the cost of production of the ball without affecting overall performance of the finished ball. Furthermore, polar-group modified rubbers can be blended with ionomers as described, for example, in commonly assigned U.S. Pat. Nos. 4,986,545; 5,098,105; 5,187,013; 5,303,837 and 5,338,610, all of which are herein incorporated by reference. Examples of thermoplastic elas-
omers which act as hardening or softening agents, include polyurethane, a polyester elastomer such as that sold by DuPont as Hytrel®, a polyester polyurethane such as B. F. Goodrich Company’s Estane® polyester polyurethane X-4517, and a polyester amide such as that sold by Elf Atochem S. A. under the name Pebax®. A plastomer such as that sold by Exxon under the name Exact™, e.g., Exact™ 4049 can be included. Various plasticizers and processing aids also can be used. It may also be preferred to apply a conventional clear coat on the cover layer.

When the golf ball of the invention has more than two cover layers, the inner cover layer as defined in this application can be formed from two or more layers which, taken together, meet the requirements of softness, thickness and compression of the layer or layers which are defined herein as the inner cover layer. Similarly, the outer cover layer can be formed from two or more layers which, taken together, meet the requirements of hardness, thickness and compression of the layer or layers which are defined herein as the outer cover layer. Furthermore, one or more additional, very thin ionomeric or non-ionomeric layers can be added on either side of the inner cover layer as long as the objectives of the invention are achieved.

An extensive discussion of compositions, materials, processes and equipment for forming covers for the preferred embodiment golf balls of the present invention is set forth in U.S. Pat. Nos. 5,833,443; 5,830,087; 5,827,167; 5,820,489; 5,820,488; 5,803,831; 5,800,284; 5,779,562; 5,779,561; and 5,733,207, all of which are hereby incorporated by reference.

**Outermost Cover Layer**

In accordance with the present invention, a thin outermost cover layer of a scuff resistant and/or scratch resistant material is disposed on the outer surface of a golf ball.

In a preferred embodiment of the present invention, this thin outermost cover layer is disposed on the outer surface of the cover 3 of the golf ball 1 illustrated in FIG. 1; on the outer surface of the outer cover layer 18 of the golf ball 10 of FIG. 2; on the outer layer 28 of the golf ball 20 of FIG. 3; and on the outer layer of the cover 38 of the golf ball 30 of FIG. 4.

In another preferred embodiment of the present invention, the outer layer of a multi-layer cover assembly is formed, as described herein, to serve as the outermost protective layer. For example, the outer cover layer 18 of the multi-layer cover assembly illustrated in FIG. 2, may be formed to serve as the outermost protective layer.

The noted very thin protective outermost layer has a maximum thickness such that the layer does not detract from the playability, i.e., spin, feel, etc., of the golf ball, as compared to the ball if not having this layer. The thickness of this outermost layer is preferably less than about 0.040 inches, more preferably less than about 0.025 inches, and most preferably less than about 0.020 inches. The minimum thickness for this outermost cover layer is that thickness at which the layer provides an effective degree of scuff and/or scratch resistance for the golf ball.

A wide array of materials may be used for this very thin outermost cover layer. Preferred compositions include ionomer blends such as Spalding Blends No. 1 and 2, set forth below.

<table>
<thead>
<tr>
<th>Materials</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surylon® 8320</td>
<td>17.4</td>
</tr>
<tr>
<td>Surylon® 8320</td>
<td>7.6</td>
</tr>
<tr>
<td>Surylon® 8540</td>
<td>49.0</td>
</tr>
<tr>
<td>Surylon® 8540</td>
<td>16.4</td>
</tr>
<tr>
<td>2832-2</td>
<td>9.6</td>
</tr>
<tr>
<td>White MB</td>
<td>—</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Spalding Blend No. 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surylon® 8320</td>
</tr>
<tr>
<td>Surylon® 8120</td>
</tr>
<tr>
<td>Surylon® 8120</td>
</tr>
<tr>
<td>Surylon® 8540</td>
</tr>
<tr>
<td>2832-2</td>
</tr>
<tr>
<td>White MB</td>
</tr>
</tbody>
</table>

Other preferred materials include harder materials such as high acid blends, thermoplastic polyurethane, thermoset polyurethane, and combinations thereof. Additional materials contemplated for use in the outer layer include polyamide, SEBS, PPE, metallocones, and combinations thereof. Moreover, the compositions and combinations of materials described in the disclosure for the cover above can be used to form the outermost cover layer as long as the objectives of the present invention are met. The properties of the outer layer may be further improved by electron beam or gamma radiation treatment, as described in U.S. Pat. No. 5,891,973, herein incorporated by reference.

The hardness of the outermost cover layer also dictates the golf ball’s durability and playability. In a preferred embodiment of this invention, the Shore D hardness of the outer cover layer is at least 56, more preferably at least 60, and most preferably at least 62. The maximal Shore D hardness is one which provides maximum durability without decreasing the playability properties of the golf ball. Preferably, the Shore D hardness of the outermost cover layer is greater than the Shore D hardness of the layer below it.

**EXAMPLES**

Having generally described the invention, the following examples are included for purposes of illustration so that the invention may be more readily understood and are in no way intended to limit the scope of the invention unless otherwise specifically indicated.

**Comparative Example 1**

About 2 dozen thermoset polybutadiene golf ball cores having a conventional composition, a PGA compression of 93, a COR of 0.782 and a diameter of 1.47 inches were molded in a conventional manner. An inner cover layer of a first ionomer formed from a blend of a soft acrylic acid based ionomer containing a softening comonomer and an acrylate acid based ionomer, designated as ionomer 1, having a thickness of 0.050 inches, and a Shore D hardness of 55 was injection molded over the cores. The resulting covered cores had a PGA compression of 94 and a COR of 0.789.
An outer layer formed from a blend of two hard acrylic acid based ionomers and designated as ionomer 2 was injection molded over the inner layer. The outer layer had a thickness of 0.055 inches and a Shore D hardness of 68. The balls were primed and clear coated in a uniform manner. The balls with the two-part cover had an average PGA compression of about 99, and a COR of about 0.803. The spin rate of the balls was determined by striking the balls with a 9-iron under conditions of launch angle, ball speed, and tee position, which produced a spin rate of about 7100 rpm for a two-piece hard covered ball (1994 Top-Flite XL), and a spin rate of about 9700 rpm for a thread wound balata covered ball (1994 Titleist Tour 100) using the same club. The properties of the balls are shown in Table 1.

### Example 1

Same as Comparative Example 1 except that the outer cover layer was 0.025 inches thick instead of 0.055 inches. The resulting ball is predicted to have a PGA compression of about 90 (softened), a COR of 0.803 (unchanged), a spin rate of 8000 (increased), and a scuff resistance that is excellent and at least as good as compared to the thicker cover version.

### Comparative Examples 2-4

The procedure of Comparative Example 1 was repeated using three different combinations of inner and outer cover layer materials at the same cover layer thicknesses. The results are shown on Table 1.

### Example 2

The ball configuration was the same as Comparative Example 3 except that the outer cover layer thickness was reduced to 0.025 inches. The resulting ball is predicted to have a PGA compression of 90 (softer feel), a COR of 0.809 (unchanged), a spin rate of 7000, and excellent cut and scuff resistance that is at least as good as compared to the thicker cover version.

### Table 1

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Size (inches)</th>
<th>COMP (PGA)</th>
<th>(if readily available)</th>
<th>COR&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Material</th>
<th>Thickness (inches)</th>
<th>COMP&lt;sup&gt;2&lt;/sup&gt;</th>
<th>COR&lt;sup&gt;3&lt;/sup&gt;</th>
<th>Hardness (Shore D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. 1</td>
<td>1.47</td>
<td>93</td>
<td></td>
<td>782</td>
<td>Ionomer 1</td>
<td>0.050</td>
<td>94</td>
<td>799</td>
<td>55</td>
</tr>
<tr>
<td>1</td>
<td>1.47</td>
<td>93</td>
<td></td>
<td>782</td>
<td>Ionomer 2</td>
<td>0.050</td>
<td>94</td>
<td>799</td>
<td>55</td>
</tr>
<tr>
<td>Comp. 2</td>
<td>1.47</td>
<td>93</td>
<td></td>
<td>782</td>
<td>Ionomer 3</td>
<td>0.050</td>
<td>94</td>
<td>795</td>
<td>63</td>
</tr>
<tr>
<td>Comp. 3</td>
<td>1.47</td>
<td>93</td>
<td></td>
<td>782</td>
<td>Ionomer 1</td>
<td>0.050</td>
<td>94</td>
<td>799</td>
<td>55</td>
</tr>
<tr>
<td>Comp. 4</td>
<td>1.47</td>
<td>93</td>
<td></td>
<td>782</td>
<td>Ionomer 2</td>
<td>0.050</td>
<td>94</td>
<td>795</td>
<td>63</td>
</tr>
<tr>
<td>2</td>
<td>1.47</td>
<td>93</td>
<td></td>
<td>782</td>
<td>Ionomer 1</td>
<td>0.050</td>
<td>94</td>
<td>799</td>
<td>55</td>
</tr>
</tbody>
</table>

1.<sup>Actual COR values have been multiplied by 1000</sup>
2.<sup>COMP of inner cover layer and core</sup>
3.<sup>COR of inner cover layer and core</sup>
4.<sup>Estimated values</sup>

### Comparative Example 5

A golf ball core made of a blend of polybutadiene, zinc diacrylate, zinc dimethacrylate, and conventional additives, and having a diameter of 1.43 inches was obtained. The core had a COR of 0.763. The core was coated with a polyolefin material in a thickness of 0.058 inches. The polyolefin material was a butene comonomer with a melt index of 4.5 dg/min and is available under the unregistered trademark EXACT<sup>TM</sup> 4049 (Exxon Chemical Company, Houston, Tex.).

An outer cover layer formed from a blend of ionomers designated as ionomer 1 was used for the cover of the ball and was injection molded over the inner cover layer in a thickness of 0.090 inches. The outer cover layer had a Shore D hardness of 68 (ASTM D-2240).

The resulting golf ball was primed and top coated using conventional materials. The resulting ball had a coefficient of restitution of 0.796, and a PGA compression 79. The properties of the core, cover layers, and overall golf ball are shown on Table 2.
Comparative Examples 6-9

[0103] The procedure of Comparative Example 5 was repeated using different combinations of inner cover layer thickness and core size and composition. The same types of inner and outer cover layer materials were used in Comparative Examples 6-9 as were used in Comparative Example 5. The results are shown on Table 2.

[0104] As shown by Comparative Examples 5-9, golf balls having a good coefficient of restitution and soft compression can be obtained even when the inner cover layer is not an ionomer or balata. Surprisingly, the relative thicknesses of the inner cover layer and outer cover layer had little impact on COR. The balls of Comparative Example 9 exhibited a high COR, while having a thick inner cover layer and a soft compression. The balls of Comparative Example 7 have a relatively high COR in combination with a soft inner cover layer and a low spin rate.

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Core Material</th>
<th>Core Size (inches)</th>
<th>COMP (PGA)</th>
<th>COR (x1000)</th>
<th>Inner Cover Layer Thickness (inches)</th>
<th>COMP (PGA)</th>
<th>COR (x1000)</th>
<th>Hardness (Shore D)</th>
<th>Thickness (inches)</th>
<th>COMP (PGA)</th>
<th>COR (x1000)</th>
<th>Weight (g)</th>
<th>SPIN (RPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. 5</td>
<td>PB2, BL1</td>
<td>1.43 - 2</td>
<td>763</td>
<td>0.058</td>
<td>58</td>
<td>763</td>
<td>30</td>
<td>0.090</td>
<td>79</td>
<td>794</td>
<td>45.9</td>
<td>9</td>
<td>7945</td>
</tr>
<tr>
<td>Comp. 6</td>
<td>PB2, BL1</td>
<td>1.43 - 2</td>
<td>763</td>
<td>0.070</td>
<td>55</td>
<td>761</td>
<td>30</td>
<td>0.075</td>
<td>78</td>
<td>794</td>
<td>43.8</td>
<td>7945</td>
<td>7945</td>
</tr>
<tr>
<td>Comp. 7</td>
<td>PB2, BL2</td>
<td>1.47 - 90</td>
<td>789</td>
<td>0.050</td>
<td>82</td>
<td>787</td>
<td>30</td>
<td>0.0765</td>
<td>93</td>
<td>806</td>
<td>44.9</td>
<td>7736</td>
<td></td>
</tr>
<tr>
<td>Comp. 8</td>
<td>PB2, BL2</td>
<td>1.43 - 788</td>
<td>788</td>
<td>0.058</td>
<td>75</td>
<td>785</td>
<td>30</td>
<td>0.090</td>
<td>89</td>
<td>817</td>
<td>44</td>
<td>8039</td>
<td></td>
</tr>
<tr>
<td>Comp. 9</td>
<td>PB2, BL2</td>
<td>1.43 - 788</td>
<td>788</td>
<td>0.070</td>
<td>70</td>
<td>784</td>
<td>30</td>
<td>0.075</td>
<td>83</td>
<td>803</td>
<td>45.8</td>
<td>8039</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>PB2, BL1</td>
<td>1.43 - 763</td>
<td>763</td>
<td>0.070</td>
<td>55</td>
<td>761</td>
<td>30</td>
<td>0.025</td>
<td>65</td>
<td>794</td>
<td>45.8</td>
<td>85005</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>PB2, BL1</td>
<td>1.43 - 788</td>
<td>788</td>
<td>0.058</td>
<td>75</td>
<td>785</td>
<td>30</td>
<td>0.025</td>
<td>75</td>
<td>817</td>
<td>45.8</td>
<td>85005</td>
<td></td>
</tr>
</tbody>
</table>

1Polybutadiene blend 1
2Polybutadiene blend 2
3Estimated values

Example 3

[0105] The ball configuration was the same as Comparative Example 8 except that the outer cover layer thickness was reduced to 0.025 inches. The PGA compression softened to 65, the COR relatively unchanged at 0.794, the spin rate increased to 8500, and the cut and scuff resistance remained excellent.

Example 4

[0106] The ball configuration was the same as Comparative Example 9 except that the outer cover layer thickness is reduced to 0.025 inches. The PGA compression softened to 75, the COR unchanged at 0.807, the spin rate increased to 8500, and the cut and scuff resistance remained excellent.

Comparative Examples 10-12

[0107] Three golf balls, labeled Comparative Examples 10, 11, and 12, respectively, were formed with the same core composition. The three golf balls contained no mantle layer. Each ball was molded with a different cover.

[0108] The outer cover layer of Comparative Example 10 was made from 90.6 parts by weight Iotek 7510 and 9.4 parts White MB. The outer cover layer of Comparative Example 11 was made from 57.6 parts Iotek 7510, 33 parts Iotek 8000, and 9.4 parts White MB. The outer cover layer of Comparative Example 12 was made from 35 parts Surlyn® 8140, 57.5 parts Surlyn® 6120, and 12.5 parts White MB.

[0109] A "Guillotine Cut Test" was performed on the golf balls by holding the ball firmly in the cavity to expose the top half of the ball. A guillotine blade weighing 5 pounds and having inner and outer blade edge angles of 900 and 600, respectively, and a cutting edge of three sixty-fourths inch radius was dropped from a height of 3.5 feet to strike the ball at a point one-half inch off the top center point. The guillotine blade was guided during the drop by means of a substantially friction-free vertical track. The drops were repeated until ball failure occurred, ball failure defined as permanent damage evidenced by a crack or by removal of a segment from the ball surface.

Example 5

[0110] A multi-layered golf ball was made with the same core as the golf balls found in Comparative Examples 10-12. The inner cover layer of the multi-layered ball is constructed by molding Iotek 7510, having a Shore D hardness of about 45, over the core using a 1.68 inch injection mold. The composition of the mantle layer of the multi-layered golf ball is the same as the outer cover layer of Comparative Example 10 except for the addition of White MB to the outer cover layer composition of Comparative Example 10. The core and inner cover were galvanized to a size of approximately 1.645", thus leaving a mantle thickness of about 0.050". Alternatively, the mantle could have been molded either by compression or injection molding in the proper size cavities to yield the desired mantle size and thickness.
After glebar, a very thin, hard layer of ionomer made from 55 parts by weight Surlyn® 8140, 57.5 parts multi-layered ball were much better than those found in Comparative Examples 10 and 11.

### TABLE 3

<table>
<thead>
<tr>
<th>Example No.</th>
<th>CORE</th>
<th>MANTLE LAYER</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Size</td>
<td>Weight (g)</td>
</tr>
<tr>
<td>10</td>
<td>1.54&quot;</td>
<td>36.8</td>
</tr>
<tr>
<td>11</td>
<td>1.54&quot;</td>
<td>36.8</td>
</tr>
<tr>
<td>12</td>
<td>1.54&quot;</td>
<td>36.8</td>
</tr>
<tr>
<td>5</td>
<td>1.54&quot;</td>
<td>36.8</td>
</tr>
<tr>
<td>6</td>
<td>1.54&quot;</td>
<td>36.8</td>
</tr>
</tbody>
</table>

### OUTER COVER LAYER

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Shore C/D</th>
<th>Cover Material</th>
<th>Thickness (g)</th>
<th>Weight (g)</th>
<th>Comp</th>
<th>COR</th>
<th>Shore C/D</th>
<th>Guillotine (rank)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>—</td>
<td>C³</td>
<td>0.070*</td>
<td>45.4</td>
<td>86</td>
<td>0.780</td>
<td>70/45</td>
<td>1.5 5th</td>
</tr>
<tr>
<td>11</td>
<td>—</td>
<td>D⁴</td>
<td>0.070*</td>
<td>45.3</td>
<td>81</td>
<td>0.787</td>
<td>84/56</td>
<td>1.5 4th</td>
</tr>
<tr>
<td>12</td>
<td>—</td>
<td>E⁵</td>
<td>0.070*</td>
<td>45.4</td>
<td>66</td>
<td>0.811</td>
<td>97/71</td>
<td>1 1st</td>
</tr>
<tr>
<td>5</td>
<td>70/45</td>
<td>E</td>
<td>0.021*</td>
<td>45.6</td>
<td>80</td>
<td>0.790</td>
<td>85/57</td>
<td>1 2nd</td>
</tr>
<tr>
<td>6</td>
<td>84/54</td>
<td>E</td>
<td>0.021*</td>
<td>45.6</td>
<td>75</td>
<td>0.794</td>
<td>91/80</td>
<td>1 3rd</td>
</tr>
</tbody>
</table>

A¹ = 300 pts lotek 7510  
B² = 60 pts lotek 7510; 33 pts lotek 8000; 7 pts lotek 7030  
C³ = 90.6 pts lotek 7510; 9.4 pts White MB  
D⁴ = 57.6 pts lotek 7510; 33 pts lotek 8000; 9.4 pts White MB  
E⁵ = 35 pts Surlyn® 8140; 57.5 pts Surlyn® 6120; 12.5 pts White MB

Surlyn® 6120, and 12.5 parts White MB, having a Shore D hardness of 70-71, was compression molded over the soft mantle. The outer cover layer of the multi-layered golf ball was the same composition as the outer cover layer of Comparative Example 12. The outer cover thickness for the multi-layered golf ball is about 0.020". A Guillotine Cut Test was then performed on the ball.

The outer cover layer of the multi-layered golf ball has a Shore D hardness of 70, while the inner cover layer has a Shore D hardness of about 45. The overall Shore D hardness measured on the ball was 57, roughly in between the Shore D hardness measurements of the inner and outer cover layers.

The multi-layered golf ball was faster and better for cut resistance compared to Comparative Examples 10 and 11. Comparative Example 12 did have a higher Guillotine resistance than the multi-layered golf ball, but this result was expected due to the high cover hardness and compression as well as greater overall thickness of the outer cover layer.

**Example 6**

The configuration for the multi-layered golf ball was the same as Example 5 except that the inner cover layer was made from 60 parts by weight lotek 7510, 33 parts lotek 8000, and 7 parts 7030. The Shore D hardness of the outer cover layer was 70, while the Shore D hardness of the inner cover layer was about 54. The overall Shore D hardness of the cover was about 60, roughly halfway between the inner and outer cover layer hardness. The guillotine results of the

While certain representative embodiments and details of the present invention have been shown for the purposes of illustrating the invention, it will be apparent to those skilled in the art that various changes and modifications may be made therein without departing from the spirit or scope of the invention.

Having thus described the preferred embodiment, the invention is now claimed to be:

1. A golf ball comprising:
   a core; and
   a cover enclosing said core, wherein said cover includes at least one layer comprising an outermost layer having a thermoplastic material, a thickness of less than about 0.040 inches, a Shore D hardness of at least about 56 and a Shore D hardness at least as hard as a layer disposed between said outermost layer and said core.

2. The golf ball according to claim 1, wherein said golf ball further comprises a mantle layer disposed between said core and said cover.

3. The golf ball according to claim 1, wherein said outermost layer comprises an ionomer.

4. The golf ball according to claim 1, wherein said outermost layer comprises a high acid ionomer consisting of (i) an olefin having 2 to 8 carbon atoms, and (ii) an unsaturated monocarboxylic acid having 3 to 8 carbon atoms.

5. The golf ball according to claim 1, wherein said outermost layer has a Shore D hardness of at least about 60.
6. The golf ball according to claim 1, wherein said outermost layer has a Shore D hardness of at least about 62.
7. The golf ball according to claim 1, wherein said outermost layer has a thickness of less than about 0.025 inches.
8. The golf ball according to claim 1, wherein said outermost layer has a thickness of less than about 0.020 inches.
9. The golf ball according to claim 1, wherein said cover further includes an inner layer and said outermost layer is disposed about said inner layer.
10. A golf ball comprising:
    a core; and
    a cover comprising an inner layer and an outermost layer disposed about said inner layer, said outermost layer comprising a thermoplastic material, having a thickness of less than about 0.040 inches, a Shore D hardness of at least 56 and a Shore D hardness at least as hard as said inner layer.
11. The golf ball according to claim 10, wherein said golf ball further comprises a mantle layer disposed between said core and said cover.
12. The golf ball according to claim 10, wherein said outermost layer comprises an ionomer.
13. The golf ball according to claim 10, wherein said outermost layer comprises a high acid ionomer consisting of (i) an olefin having 2 to 8 carbon atoms, and (ii) an unsaturated monocarboxylic acid having 3 to 8 carbon atoms.
14. The golf ball according to claim 10, wherein said outermost layer has a Shore D hardness of at least about 60.
15. The golf ball according to claim 10, wherein said outermost layer has a Shore D hardness of at least about 62.
16. The golf ball according to claim 10, wherein said outermost cover layer has a thickness of less than about 0.025 inches.
17. The golf ball according to claim 10, wherein said outer cover layer has a thickness of less than about 0.020 inches.
18. A golf ball comprising:
    a core; and
    a cover, wherein said cover includes an outermost layer that comprises a thermoplastic material, said outermost layer having a thickness less than about 0.040 inches, a Shore D hardness at least about 56 and a Shore D hardness at least as hard as a layer disposed between said outermost layer and said core.
19. The golf ball according to claim 18, wherein said golf ball comprises a mantle layer disposed between said core and said cover.
20. The golf ball according to claim 19, wherein said mantle layer is disposed between said core and said wound layer.
21. The golf ball according to claim 18, wherein said outermost layer comprises an ionomer.
22. The golf ball according to claim 18, wherein said outermost layer comprises a high acid ionomer consisting of (i) an olefin having 2 to 8 carbon atoms, and (ii) an unsaturated monocarboxylic acid having 3 to 8 carbon atoms.
23. The golf ball according to claim 18, wherein said outermost layer has a Shore D hardness of at least about 60.
24. The golf ball according to claim 18, wherein said outermost layer has a Shore D hardness of at least about 62.
25. The golf ball according to claim 18, wherein said outermost layer has a thickness less than about 0.025 inches.
26. The golf ball according to claim 18, wherein said outermost layer has a thickness less than about 0.020 inches.
27. The golf ball according to claim 18, wherein said cover further includes an inner layer disposed immediately adjacent to said outermost layer and between said core and said outermost layer.

* * * * *