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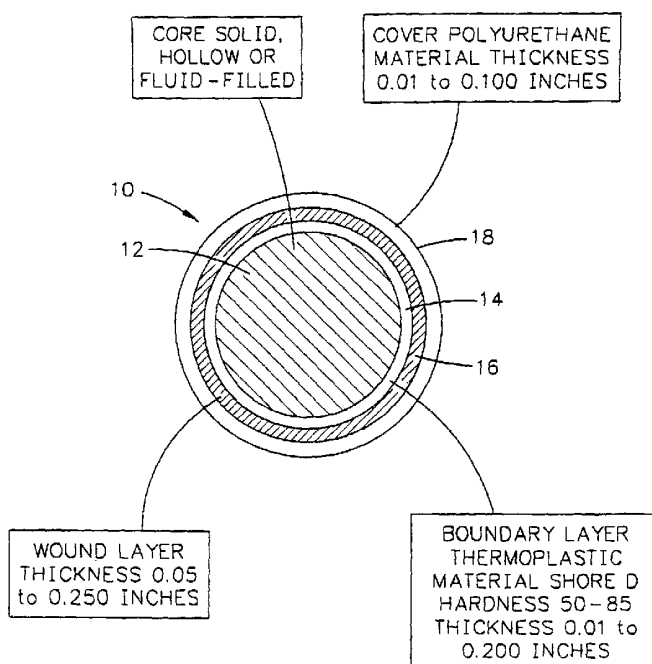
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(54) Title: MULTIPLE PIECE GOLF BALL



(57) **Abstract:** A multiple piece golf ball (10) is disclosed herein. The golf ball (10) preferably has a core (12) with an oxygen barrier boundary layer (14), a wound layer (16) and a polyurethane cover (18). The core (12) is preferably composed of polybutadiene material. The boundary layer (14) is preferably composed of a blend of ionomers. The cover (18) is preferably composed of a thermosetting polyurethane material. The golf ball (10) has exceptional distance, exceptional feel and exceptional durability.



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Title

MULTIPLE PIECE GOLF BALL

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Technical Field

The present invention relates to a multiple layer golf ball. More specifically, the present invention relates to a multiple-piece golf ball wherein the golf ball has a core, a boundary layer, an optional wound layer and a cover.

10

Background Art

Golf balls have evolved throughout the history of the game. The first type of golf balls were the “featherie”, a leather sphere stuffed with wet, compressed feathers. The next innovation in golf balls was the gutta percha one piece golf ball. As early as the 1800’s, golfers realized that gutta percha golf balls with indented surfaces
15 flew better than those with smooth surfaces. Hand-hammered gutta-percha golf balls could be purchased at least by the 1860’s, and golf balls with brambles (bumps rather than dents) were in style from the late 1800’s to 1908. In 1908, an Englishman, William Taylor, received a patent for a golf ball with indentations (dimples) that flew better and more accurately than golf balls with brambles. A.G. Spalding & Bros.,
20 purchased the U.S. rights to the patent and introduced the GLORY ball featuring the TAYLOR dimples. Until the 1970s, the GLORY ball, and most other golf balls with dimples had 336 dimples of the same size using the same pattern, the ATTI pattern. The ATTI pattern was an octohedron pattern, split into eight concentric straight line rows, which was named after the main producer of molds for golf balls. The only

innovation related to the surface of a golf ball during this sixty year period came from Albert Penfold who invented a mesh-pattern golf ball for Dunlop. This pattern was invented in 1912 and was accepted until the 1930's.

Golf balls with a wound layer appeared in the 1920's, and have been refined
5 since that time. In the 1930's through the 1960's, the major innovations in golf balls related to core development. In the 1960's, the development of ionomer materials, particularly the brand SURLYN® from Du Pont, became the major innovation for golf balls into the 1980's. In the 1970's, dimple pattern innovations also appeared from the major golf ball manufacturers. In 1973, Titleist introduced an icosahedron pattern
10 which divides the golf ball into twenty triangular regions. In the late 1980's and into the 1990's, three-piece solid golf balls, as opposed to three-piece wound, began to appear from the major golf ball manufacturers. These three-piece solid golf balls involved two thermoplastic layers covering a core.

Although not commercialized, several patents have disclosed four-piece golf
15 balls. One example is Sun, U.S. Patent Number 5,273,286 for a Multiple Concentric Section Golf Ball, which was filed in 1992. Sun discloses a golf ball with a solid inner core, a graphite intermediate core, a polybutadiene outer core and a cover composed of balata, ionomer or urethane materials.

Other examples are Hayashi *et al.*, U.S. Patent Number 5,816,940 for a Wound
20 Golf Ball, which was originally filed in Japan in 1996, and Hayashi *et al.*, U.S. Patent Number 5,797,808 for a Wound Golf Ball which was originally filed in Japan in 1996. The Hayashi patents disclose a polybutadiene center core, a thermoplastic enclosure layer (preferably an elastomer), a wound layer and a cover composed of an inner layer and an outer layer with both cover layers composed of thermoplastic materials.

Yet another example is Maruko *et al.*, U.S. Patent Number 5,674,137 which was originally filed in Japan in 1994. Maruko discloses a golf ball with a liquid filled core, a wound layer over the core, and inner and outer cover layers composed of an ionomer material. The primary objective of Maruko is to provide a golf ball with good distance,
5 well-defined spin and greater durability.

A further example is Yabuki *et al.*, U.S. Patent Number 5,716,293 for a Golf Ball which was originally filed in Japan in 1995. Yabuki discloses a golf ball with a rubber solid core containing an oil substance, an oil-resistant coating layer, a wound layer and an ionomer cover layer.

10 Another example is Stanton *et al.*, U.S. Patent Number 5,836,831 for a Golf Ball, originally filed in 1996. Stanton discloses a liquid filled core having a polyether-amide shell, a wound layer and a polymer cover.

There have been many attempts to develop a golf ball that can do everything for every golfer, a golf ball that has tremendous distance, with exceptional feel and
15 outstanding durability. However, current golf balls have been unable to deliver everything.

Disclosure of the Invention

20 The present invention provides a golf ball that has tremendous distance, with exceptional feel and outstanding durability. The present invention is able to accomplish this by providing a four-piece wound golf ball with a polyurethane cover.

One aspect of the present invention is a golf ball having a core, a boundary layer, a wound layer and a cover. The boundary layer covers the core and is a
25 thermoplastic material having a Shore D hardness between 40 and 85. The wound layer

covers the boundary layer. The cover is preferably a polyurethane material, and it covers the wound layer.

Another aspect of the present invention is method for manufacturing a four-piece golf ball. The method includes injection molding a boundary layer over a core.

- 5 The boundary layer is a thermoplastic material having a Shore D hardness in the range of 40 to 85. The method also includes winding a fiber around the boundary layer to form a wound layer. The method also includes forming a polyurethane layer over the wound layer to form the four-piece golf ball.

- Yet another aspect of the present invention is a four-piece golf ball having a
10 solid core, a thermoplastic boundary layer, a wound layer and a thermosetting polyurethane cover. The solid core includes a polybutadiene material, has a PGA compression of at least 80, and a diameter in the range of 1.35 inches to 1.58 inches. The boundary layer covers the solid core and is composed of blend of ionomer materials. The boundary layer also has a Shore D hardness between 40 and 85, and a
15 thickness in the range of 0.01 inches to 0.1 inches. The wound layer covers the boundary layer, and has a thickness of 0.05 to 0.1 inches. The thermosetting polyurethane layer covers the wound layer, and has a thickness in the range of 0.01 inches to 0.05 inches.

- The primary object of the present invention is to provide a golf ball that can
20 deliver exceptional distance with exceptional feel and exceptional durability.

Brief Description of the Drawings

FIG. 1 is a cross-section view of a four-piece golf ball of the present invention.

FIG. 2 is a cross-sectional view of an alternative embodiment of a four-piece golf ball of the present invention.

5

Best Mode(s) For Carrying Out The Invention

The novel golf ball of the present invention provides greater distance, better feel, and outstanding durability than present golf balls. The present invention is able to achieve this by providing a four-piece golf ball having a high energy core for distance, a boundary layer to prevent degradation of the core, a wound layer for feel and a polyurethane cover for durability.

As illustrated in FIG. 1, the golf ball of the present invention is generally indicated as 10. The golf ball 10 preferably includes a solid core 12, a boundary layer 14, a wound layer 16 and a cover 18. Alternatively, as shown in FIG. 2, the golf ball 10 may include a fluid-filled core 12', a boundary layer 14, a wound layer 16, and a cover 18. The boundary layer 14 that covers the core 12 has a predetermined hardness that is softened by the wound layer 16 and the relatively soft cover 18. Alternatively, the golf ball 10 of the present invention includes a solid core, a boundary layer, an optional wound layer 16 and a cover 18.

20 The cover 18 is a polyurethane cover that is relatively soft and has a good durability due to the high resilience of the polyurethane material. The polyurethane

cover 18 is composed of a polyurethane material preferably formed from a blend of diisocyanate prepolymers. Preferably, the polyurethane is a thermosetting polyurethane, however, thermoplastic polyurethane materials are within the scope of the present invention. The blend of diisocyanate prepolymers includes at least one

5 TDI-based polyurethane prepolymer and at least one other diisocyanate-based polyurethane prepolymer. In a preferred embodiment, the blend of diisocyanate prepolymers includes at least one PPDI-based polyurethane prepolymer and at least one TDI-based polyurethane prepolymer. Alternative embodiments have a blend which includes at least two different PPDI-based polyurethane prepolymer and at least one

10 TDI-based polyurethane prepolymer. Yet further embodiments may include at least one TDI-based polyurethane prepolymer and at least one MDI-based polyurethane prepolymer. Still further embodiments have only a PPDI-based prepolymer instead of a blend of polyurethane prepolymers. Those skilled in the pertinent art will recognize that multiple variations of diisocyanate prepolymers may be utilized without departing

15 from the scope and spirit of the present invention. The cover 18 is described in greater detail below.

In a preferred embodiment, the polyurethane cover 18 encompasses the wound layer 16. In an alternative embodiment, the cover 18 encompasses boundary layer 14. The wound layer 16 has a thickness in the range of 0.050 inches to 0.250 inches,

20 preferably in the range of 0.060 inches to 0.150 inches and most preferably in the range of 0.080 to 0.100 inches. A preferred embodiment has a wound layer 16 with a

thickness of 0.080 inches. The wound layer 16 is preferably an elastic fiber having a predetermined modulus of elasticity. A preferred elastic fiber is a rubber thread with a cross section of approximately 0.022 inches x 0.0625 inches, and an ultimate elongation of approximately 1000 grams (the thread has a 1000% elongation under a load of 1000
5 grams). Devices for winding threads around cores are well known in the golf industry. One such apparatus rotates a golf ball core as it draws thread through a tensioning system from a thread source. The tensioning system usually has several tension wheels for applying tension to the thread during winding around the core. The thread is wound around the core to a predetermined diameter. In constructing the golf ball 10 of the
10 present invention, a similar winding device winds the thread around the boundary layer 14 and core 12.

The wound layer 16 provides a softer feel to the golf ball 10, especially with a solid polybutadiene core 12. The wound layer 16 also provides a golf ball 10 with better spin around the greens while not deterring from the distance performance.

15 The threads of the wound layer 16 encompass a boundary layer 14, as shown in FIGS. 1 and 2. The boundary layer 14 is preferably composed of a thermoplastic material that has a predetermined hardness. A preferred material for the boundary layer 14 is a blend of ionomers such as those sold by DuPont under the brand name SURLYN® or those sold by Exxon Chemical under the brand name IOTEK®.
20 Alternatively, the boundary layer 14 may be composed of a polyether block amide such as PEBAX®, or a polyester elastomer such as HYTREL®. The boundary layer has a

Shore D hardness, as measured by ASTM standards, in range of 55 to 75, preferably 65 to 75, and most preferably 70. The boundary layer 14 is described in greater detail below.

The boundary layer 14 encompasses the core 12. As mentioned above, the core
5 12 may be solid, hollow, or fluid filled with a liquid or gas. A preferred core 12 is a solid core primarily composed of a polybutadiene material. The fluid filled version of the core 12 is preferably filled with a liquid such as corn syrup or water. The core 12 is described in greater detail below.

The core 12, boundary layer 14, wound layer 16 and cover 18 construction
10 creates a golf ball 10 that has exceptional overall properties, and has the best performance in many if not all pertinent categories. The positioning of a wound layer 16 over a relatively hard boundary layer 14 with a relatively soft and durable cover 18 creates a unique golf ball 10 that has a good feel and delivers tremendous distance.

As mentioned previously, a preferred material for the cover 18 is a
15 thermosetting polyurethane material. The preferred polyurethane is composed of blend of a TDI-based prepolymer, a second diisocyanate-based polyurethane prepolymer and a curing agent. The TDI-based prepolymer is preferably formed from TDI and a polyether polyol. The second diisocyanate-based polyurethane prepolymer is preferably a PPDI-based prepolymer formed from PPDI and a polyester polyol,
20 preferably a polycaprolactone. The prepolymer blend is cured with a curing agent. The curing agent, or curative, may be a diol (e.g., 1,4 butane diol, trimethylpropanol), a

mixture of diols (e.g., 1,4 butane diol and ethylene glycol, or other suitable glycols), a hydroquinone, a mixture of hydroquinones, a triol, a mixture of triols, a diamine, a mixture of diamines, an oligomeric diamine, a triamine, or a blend of some or all of these materials. Preferably, the curing agent is a blend of a diamine and a mixture of
5 diols.

In an alternative embodiment, the blend of prepolymers includes three diisocyanate-based polyurethane prepolymers. In this embodiment, the TDI-based prepolymer is preferably formed from TDI and a polyether polyol. The second diisocyanate-based polyurethane prepolymer is preferably a PPDI-based prepolymer
10 formed from PPDI and a polyester polyol, preferably a polycaprolactone. The third diisocyanate-based polyurethane prepolymer is a PPDI-based prepolymer formed from PPDI and a polyether polyol. Preferably, the curing agent is a blend of a diamine and a mixture of diols. As mentioned above, alternative embodiments may have variations of the dual blend or the tri-blend, and may use a TDI-based polyurethane prepolymer with
15 other non-PPDI-based polyurethane prepolymers.

Yet another embodiment of a thermosetting polyurethane cover 18 is one that is composed of a single PPDI-based prepolymer instead of a blend. The PPDI-based polyurethane prepolymer provides a polyurethane with a high rebound at a lower hardness, greater durability and improved sound and feel. The PPDI-based prepolymer
20 is preferably cured with a 1,4 butane diol and ethylene glycol mixture. A preferred single PPDI-based prepolymer is a polycaprolactone terminated prepolymer.

The blending of a TDI-based prepolymer with other diisocyanate-based polyurethane prepolymers lowers the viscosity of the mixture, lowers the temperature of the exothermic reaction that occurs when the prepolymers are reacted with the curing agent, and increases the durability. The TDI-based prepolymer may range from 10 to 5 40 percent of the polyurethane prepolymer blend. Preferably, the TDI-based prepolymer is 30 percent of the polyurethane prepolymer blend. A preferred TDI based prepolymer is a TDI terminated polyether prepolymer available from Uniroyal Chemical Company of Middlebury, Connecticut, under the tradename ADIPRENE® LF950.

10 The dual blend and tri-blend formulations will preferably contain a PPDI terminated polyester prepolymer and/or a PPDI terminated polyether prepolymer. A preferred PPDI terminated polyester prepolymer is available from Uniroyal Chemical under the tradename ADIPRENE® LFPX 2950. A preferred PPDI terminated polyether prepolymer is available from Uniroyal Chemical under the tradename 15 ADIPRENE® LFPX 950.

The polyurethane prepolymer blend may have 10 to 40 parts of a TDI terminated polyether prepolymer blended with 60 to 90 parts of a PPDI terminated polyether prepolymer. Alternatively, the polyurethane prepolymer blend may have 10 to 40 parts of a TDI terminated polyether prepolymer blended with 60 to 90 parts of a 20 PPDI terminated polyester prepolymer. Further, the polyurethane prepolymer blend may have 10 to 40 parts of a TDI terminated polyether prepolymer blended with 5 to 90

parts of a PPDI terminated polyether prepolymer and 5 to 90 parts of a PPDI terminated polyester prepolymer. More specific blend formulations are set forth in the Examples below.

The cover 18 of the golf ball 10 of the present invention is most preferably
5 composed of a polyurethane formed from a polyurethane prepolymer blend composed of a TDI-based polyurethane prepolymer and a PPDI-based polyurethane prepolymer, and cured with a mixture of curing agents such as a diamine and a blend of 1,4 butane diol and glycols. A suitable blend of diol and glycols is available from Uniroyal Chemical under the tradename VIBRACURE® A250. A suitable diamine is toluene
10 ethylene diamine available from Albemarle Corporation of Baton Rouge, Louisiana under the tradename ETHACURE® 100. Other agents which may be utilized during the curing process include dimethylthio-2,4-toluenediamine (such as EHTACURE® 300 available from Albemarle Corporation); trimethyl glycol di-p-aminobenzoate (such as VERSALINK® 740M available from Air Products and Chemicals, Inc., Allentown,
15 PA); cyclohexane dimethanol; hydroquinone-bis-hydroxyethyl ether; phenyldiethanol amine mixture (such as VIBRACURE® A931 available from Uniroyal Chemical); methylene dianiline sodium chloride complex (such as CAYTOR® 31 available from Uniroyal Chemical); and/or prionene amine. This list of preferred agents (including chain extenders, cross-linkers and curing agents) is not meant to be exhaustive, as any
20 suitable (preferably polyfunctional) chain extender, cross-linker, or curing agent may be used.

The curing agent mixture for the cover 18 of the present invention may have numerous variations. In a preferred embodiment, the curing agent is composed of 30 to 70 parts of a diol blend such as VIBRACURE® 250 to 70 to 30 parts of a diamine such as ETHACURE® 300. Alternatively, the diamine component may be a blend of
5 different diamines such as a blend of EHTACURE® 100 and ETHACURE® 300.

The ratio of the polyurethane prepolymer blend to curing agent is determined by the nitrogen-carbon-oxygen group ("NCO") content of the polyurethane prepolymer blend. For example, the NCO content of the TDI-terminated polyether or TDI-terminated polyester is preferably in the range of 4.0% to 9.0%, while the NCO content
10 of the PPDI-terminated polyether is preferably in the range of 5.0% to 8.0%. The NCO content of the PPDI-terminated polyester is preferably in the range of 2.0% to 6.0%. The NCO content of the polyurethane prepolymer blend ranges from 2% to 8% of the polyurethane prepolymer blend. The amount of curing agent should correspond to 90% to 110% of the mol equivalence of the NCO content of the polyurethane
15 prepolymer blend. The weight ratio of the polyurethane prepolymer blend to the curing agent is preferably in the range of about 10:1 to about 30:1.

Prior to curing, the polyurethane prepolymer blend and curing agent are preferably stored separately. The polyurethane is formed by first heating and mixing the polyurethane prepolymer blend with the curing agent in a mold, and then curing the
20 mixture by applying heat and pressure for a predetermined time period. Additionally, a catalyst (e.g. dibutyl tin dilaurate, a tertiary amine, etc.) may be added to the mixture to

expedite the casting process. Specific suitable catalysts include TEDA dissolved in di propylene glycol (such as TEDA L33 available from Witco Corp. Greenwich, CT, 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
5 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 Witco Corp. or Air Products and Chemicals, Inc.) which is added to a curative such as VIBRACURE ® A250. Further, additives such as colorants may also be added to the mixture.

10 The polyurethane prepolymer blend material is preferably degassed and warmed in a first holding container prior to processing of the cover 18. The processing temperature for the polyurethane prepolymer blend is preferably in the range of about 100-220°F, and most preferably in the range of about 120-200°F. The polyurethane prepolymer blend is preferably flowable from the first holding container to a mixing
15 chamber in a range of about 200-1100 grams of material per minute, or as needed for processing. In addition, the polyurethane prepolymer blend material may be agitated in the first holding container, in the range of 0-250 rpm, to maintain a more even distribution of material and to eliminate crystallization.

In the preferred embodiment, the curing agent is a blend of a diamine such as
20 ETHACURE® 300 and a 1,4 butane diol and glycol such as VIBRACURE ® A250. As previously mentioned, other curatives may also be utilized in forming the cover 18

of the golf ball 10 of the present invention. The curing agent is preferably degassed and warmed in a second holding container prior to processing of the cover 18. The processing temperature for the curative is preferably in the range of about 50-230°F, and most preferably in the range of about 80-200°F. The curing agent is preferably

5 flowable from the second holding container to the mixing chamber in the range of about 15-75 grams of material per minute, or as needed. If a catalyst is used for processing the cover 18, then the catalyst is added to the curing agent in the second holding container to form a curative mixture. Suitable catalyst are described above. The curing agent and catalyst are agitated, in the range of about 0 to 250 rpm, to maintain an

10 even distribution of catalyst in the curative mixture in the second holding container. It is preferred that the catalyst is added in an amount in the range of about 0.25-5% by weight of the combined polyurethane prepolymer blend and curing agent. Additives may be added to the curative mixture as desired. It was discovered that hydrolytic instability of the polyurethane polymer may be avoided by the addition of a stabilizer

15 such as STABOXYL® (available from Rheinchemie, Trenton, New Jersey), in amounts of about 0.25-5% of the polyurethane.

The polyurethane prepolymer blend and curative mixture are preferably added to the common mixing chamber at a temperature in the range of about 160-220°F. A colorant material, such as, for example, titanium dioxide, barium sulfate, and/or zinc

20 oxide in a glycol or castor oil carrier, and/or other additive material(s) as are well known in the art, may be added to the common mixing chamber. The amount of

colorant material added is preferably in the range of about 0-10% by weight of the combined polyurethane prepolymer blend and curative materials, and more preferably in the range of about 2-8%. Other additives, such as, for example, polymer fillers, metallic fillers, and/or organic and inorganic fillers (e.g. polymers, balata, ionomers, etc.) may be added as well to increase the specific gravity of the polyurethane cover 18 of the present invention. It was discovered that the addition of barytes (barium sulfate) or a blend of barytes and titanium dioxide (preferably added in a carrier glycol and/or castor oil) to the mixture, in the amounts of about 0.01-30%, may add sufficient weight to the polyurethane cover 18. The added weight to the cover 18 allows for the specific gravity of the core 12 to be lowered thereby allowing for an increased resiliency of the core 12. The entire mixture is preferably agitated in the mixing chamber in the range of about 1 to 250 rpm prior to molding. A more detailed explanation of the process is set forth in this Assignee's co-pending U.S. Patent Application Number 09/296,197, entitled Golf Balls And Methods Of Manufacturing The Same, filed on April 20, 1999, which is hereby incorporated by reference in its entirety.

The core 12 of the golf ball 10 is the "engine" for the golf ball 10 such that the inherent properties of the core 12 will strongly determine the initial velocity and distance of the golf ball 10. A higher initial velocity will usually result in a greater overall distance for a golf ball. In this regard, the Rules of Golf, approved by the United States Golf Association ("USGA") and The Royal and Ancient Golf Club of Saint Andrews, limits the initial velocity of a golf ball to 250 feet (76.2m) per second (a

two percent maximum tolerance allows for an initial velocity of 255 per second) and the overall distance to 280 yards (256m) plus a six percent tolerance for a total distance of 296.8 yards (the six percent tolerance may be lowered to four percent). A complete description of the Rules of Golf are available on the USGA web page at www.usga.org.

- 5 Thus, the initial velocity and overall distance of a golf ball must not exceed these limits in order to conform to the Rules of Golf. Therefore, the core 12 for a USGA approved golf ball is constructed to enable the golf ball 10 to meet, yet not exceed, these limits.

The coefficient of restitution ("COR") is a measure of the resilience of a golf ball.

- The COR is a measure of the ratio of the relative velocity of the golf ball after direct
10 impact with a hard surface to the relative velocity before impact with the hard surface. The COR may vary from 0 to 1, with 1 equivalent to a completely elastic collision and 0 equivalent to a completely inelastic collision. A golf ball having a COR value closer to 1 will generally correspond to a golf ball having a higher initial velocity and a greater overall distance. The effect of a higher COR value is apparent when a golf club strikes
15 the golf ball 10. The force of the club during a swing is transferred to the golf ball 10. If the golf ball has a high COR (more elastic), then the initial velocity of the golf ball will be greater than if the golf ball had a low COR. In general, a higher compression core will result in a higher COR value.

- The core 12 of the golf ball 10 is preferably composed of a blend of a base
20 rubber, a cross-linking agent, a free radical initiator, and one or more fillers or processing aids. A preferred base rubber is a polybutadiene having a cis-1,4 content

above 90%, and more preferably 98% or above. A preferred cross-linking agent is a zinc diacrylate, and a commercially available zinc diacrylate is SR-416 from Sartomer Co., Inc., Exton, Pennsylvania. Other metal salt di- or mono- (meth)acrylates suitable for use in the present invention include those in which the metal is calcium or

5 magnesium. In the manufacturing process it may be beneficial to pre-mix some cross-linking agent(s), such as, e.g., zinc diacrylate, with the polybutadiene in a master batch prior to blending with other core components.

Free radical initiators are used to promote cross-linking of the base rubber and the cross-linking agent. Suitable free radical initiators for use in the golf ball core 12 of

10 the present invention include peroxides such as dicumyl peroxide, bis-(t-butyl peroxy) diisopropyl benzene, t-butyl perbenzoate, di-t-butyl peroxide, 2,5-dimethyl-2,5-di-5-butylperoxy-hexane, 1,1-di (t-butylperoxy) 3,3,5-trimethyl cyclohexane, and the like, all of which are readily commercially available.

Zinc oxide is also preferably included in the core formulation. Zinc oxide may

15 primarily be used as a weight adjusting filler, and is also believed to participate in the cross-linking of the other components of the core (e.g. as a coagent). Additional processing aids such as dispersants and activators may optionally be included. In particular, zinc stearate may be added as a processing aid (e.g. as an activator). Any of a number of specific gravity adjusting fillers may be included to obtain a preferred total

20 weight of the core 12. Examples of such fillers include tungsten and barium sulfate. All such processing aids and fillers are readily commercially available. A particularly

useful tungsten filler is WP102 Tungsten (having a 3 micron particle size) available from Atlantic Equipment Engineers (a division of Micron Metals, Inc.), Bergenfield, NJ.

Table 1 below provides the ranges of materials included in the preferred core formulations of the present invention.

Table 1: Core Formulations		
Component	Preferred Range	Most Preferred Range
Polybutadiene	100 parts	100 parts
Zinc diacrylate	20-35 phr	25-30 phr
Zinc oxide	0-50 phr	5-15 phr
Zinc stearate	0-15 phr	1-10 phr
Peroxide	0.2 – 2.5 phr	0.5 – 1.5 phr
Filler (e.g. tungsten)	As desired (e.g. 2-10 phr)	As desired (e.g. 2-10 phr)

In the present invention, the core components are mixed and compression molded in a conventional manner known to those skilled in the art. The finished core 12 has a diameter of about 1.20 to about 1.64 inches for a golf ball 10 having an outer diameter of 1.68 inches. More preferably, the finished core 12 has a diameter of about 1.30 to about 1.50 inches for a golf ball 10 having an outer diameter of 1.68 inches.

Most preferably, the finished core 12 has a diameter of about 1.305 to about 1.345 inches for a golf ball 10 having an outer diameter of 1.68 inches. The core weight is preferably maintained in the range of about 32 to about 40 g. The core PGA compression is preferably maintained in the range of about 55 to 90, and most preferably about 55 to 80.

As used herein, the term "PGA compression" is defined as follows:

$$\text{PGA compression value} = 180 - \text{Riehle compression value}$$

The Riehle compression value is the amount of deformation of a core or a golf ball in inches under a static load of 200 pounds, multiplied by 1000. Accordingly, for a core deformation of 0.110 inches under a load of 200 pounds, the Riehle compression value is 110 and the PGA compression value is 70.

In an alternative embodiment, the core 12 may be hollow or fluid filled. In such an embodiment, as shown in FIG. 2, the core 12 has a shell 12a encompassing an interior chamber 12b. The interior chamber may be filled with a fluid 12c. Exemplary fluids 12c are water, air, corn syrup, oil, and the like. If a liquid is utilized as the fluid 12c, then preferably the liquid occupies only half of the volume of the interior chamber 12b. The compressibility of the fluid is a primary concern in such an embodiment. The shell 12a should be sufficient to contain the fluid under the tremendous forces exerted on the shell 12a during impact between a golf club head and the golf ball 10. A preferred shell 12a is composed of a polybutadiene material. Alternatively, the shell 12a may be composed of metal such as titanium, stainless steel or the like. If the fluid

12c is air, the air may be greater or less than one atmosphere in pressure.

As is described above, the present invention includes at least one boundary layer 14 that is preferably composed of a thermoplastic material or a blend of thermoplastic materials. Most preferably the boundary layer 14 is composed of at least one

5 thermoplastic that contains organic chain molecules and metal ions. The metal ion may be, for example, sodium, zinc, magnesium, lithium, potassium, cesium, or any polar metal ion that serves as a reversible cross-linking site and results in high levels of resilience and impact resistance. Suitable commercially available thermoplastics are ionomers based on ethylene copolymers and containing carboxylic acid groups with

10 metal ions such as described above. The acid levels in such suitable ionomers may be neutralized to control resiliency, impact resistance and other like properties. In addition, other fillers with ionomer carriers may be used to modify (e.g. preferably increase) the specific gravity of the thermoplastic blend to control the moment of inertia and other like properties. Exemplary commercially available thermoplastic materials suitable for

15 use in a boundary layer 14 of a golf ball 10 of the present invention include, for example, the following materials and/or blends of the following materials: HYTREL® and/or HYLENE® products from DuPont, Wilmington, Delaware, PEBAX® products from Elf Atochem, Philadelphia, Pennsylvania, SURLYN® products from DuPont, and/or ESCOR® or IOTEK® products from Exxon Chemical, Houston, Texas.

20 The Shore D hardness of the boundary layer 14 is preferably 75. It is preferred that the boundary layer 14 have a hardness of between about 55-85 Shore D. In a

preferred embodiment, the boundary layer 14 has a Shore D hardness in the range of about 65-75. One reason for preferring a boundary layer 14 with a Shore D hardness of approximately 75 is to improve the feel of the resultant golf ball. It is also preferred that the boundary layer 14 is composed of a blend of SURLYN® ionomer resins.

5 SURLYN® 8150, 9150, and 6320 are, respectively, an ionomer resin composed of a sodium neutralized ethylene/methacrylic acid, an ionomer resin composed of a zinc neutralized ethylene/methacrylic acid, and an ionomer resin composed of a terpolymer of ethylene, methacrylic acid and n-butyl acrylate partially neutralized with magnesium, all of which are available from DuPont Polymer Products, Wilmington, Delaware.

10 The boundary layer 14 may include a predetermined amount of a baryte mixture. The baryte mixture is included as 8 or 9 parts per hundred parts of the ionomer resins. One preferred baryte mixture is composed of 80% barytes and 20% of an ionomer, and is available from Americhem, Inc., Cuyahoga Falls, Ohio, under the trade designation 38534X1. The Shore D hardness provided in Table 2 below was
15 determined according to ASTM D2240.

 Table 2 below sets forth physical data for suitable boundary layers 14 that were manufactured and incorporated into specific examples. As is shown in Table 2 below, each of the boundary layers 14 were composed of an ionomer blend and the specific percentages are provided. The thickness of each of the boundary layers 14 varies from
20 0.0525 and 0.058 inches. The Shore D hardness varies between 58 and 65, however, those skilled in the relevant art will recognize that materials for the boundary layer 14

with higher Shore D hardness values are conventional and within the scope of the invention.

TABLE 2							
Ex. No.	SURLYN®				Thickness (inches)		Shore D Hardness
	%8150	%9150	%6320				
1	40	40	20		0.058		58
2	45	45	10		0.0525		62
3	45	45	10		0.0525		62
4	40	40	20		0.058		60
5	40	40	20		0.058		60
6	40	40	20		0.058		60
7	45	45	20		0.0525		62
8	45	45	20		0.0525		62
9	50	50	0		0.0525		65
10	45	45	10		0.0525		62
11	45	45	10		0.0525		62
12	45	45	10		0.0525		62

TABLE 3

Ex.	Polyurethane prepolymer					Thickness	Shore D
No.	TDI	PPDI-1	PPDI-2	PPDI-3	PPDI-4	(inches)	Hardness
1	30	70				0.0375	47
2	30		20	50		0.0300	53
3	30				70	0.0300	47
4	30				70	0.0375	47
5	30	50	20			0.0375	47
6	30				70	0.0375	47
7	30	50	20			0.0300	47
8	30		20	50		0.0300	53
9	<u>30</u>	<u>70</u>				<u>0.0300</u>	<u>53</u>
10	20	80				0.0300	47
11	30	70				0.0300	47
12	30	70				0.0300	47

Table 3 sets forth the properties of the exemplary cover layers 18. The number of parts of each polyurethane prepolymer for each of the cover layers 18 is provided in columns 2 through 6. Column 2 includes the number of parts of the TDI-terminated polyether prepolymer, ADIPRENE® LF950. Column 3 includes the number of parts of the PPDI terminated polyether prepolymer, ADIPRENE® LFPX950. Column 4 includes the number of parts of the PPDI terminated polyester (polycaprolactone) prepolymer, ADIPRENE® LFPX2950. Column 5 includes the number of parts of the PPDI terminated polyether prepolymer, ADIPRENE® LFPX590. The difference between LFPX590 and LFPX950 is the NCO content and the molecular weight of the polyol (ether) backbone, with LFPX950 having a NCO content in the range of approximately 5.45% to approximately 5.75%, and LFPX590 having a NCO content in the range of approximately 5.6% to approximately 6.2%. Column 6 includes the number of parts of the PPDI terminated polyester (polycaprolactone) prepolymer, ADIPRENE® LFPX2952. The difference between LFPX2950 and LFPX2952 is the NCO content, with LFPX2950 having a NCO content in the range of approximately 3.55% to approximately 3.85%, and LFPX2952 having a NCO content in the range of approximately 4.45% to approximately 5.05%. Each of the polyurethane prepolymer blends for examples 1-9 and 11-12 were cured with a blend of curing agents. The blend of curing agents was composed of 50 parts ETHACURE 300 (a diamine curing agent) and 50 parts VIBRACURE A250 (a blend of a 1,4 butane diol and glycol). Example 10 of the golf balls 10 of the present invention was cured with a blend of 70 parts

ETHACURE 300 and 30 parts VIBRACURE A250. The thickness of the exemplary covers 18 is either 0.0300 inches or 0.0375 inches. The Shore D hardness of the exemplary cover layer 18 is either 47 degrees or 53 degrees.

The method initially involves forming the core 12 and the boundary layer(s) 14 of the golf ball 10 to create a golf ball precursor product. The golf ball precursor product may be the core 12 alone, or the core 12 with one or more boundary layers 14. The formation of the golf ball precursor product may be performed with conventional molding apparatuses within the same facility as the cover molding apparatus, or alternatively at an off-site location. The golf ball precursor products, whether on-site or off-site, are then transferred to a location in proximity to the cover molding apparatus. After formation of the golf ball precursor product, it is pre-heated to a predetermined temperature for a predetermined time period. The pre-heating is accomplished by applying heat to the core 12 and boundary layer(s) 14, preferably to induce thermal expansion thereof. The pre-heating of the core 12 and boundary layer(s) 14 may be achieved through any number of methods known to those skilled in the art. However, in the preferred embodiment, the core 12 and boundary layer(s) 14 are pre-heated by convection heating in an oven. An alternative means for heating the golf ball precursor product is through use of microwave heating. In microwave heating, as compared to convection heating, the surface heating of the golf ball precursor products is greatly reduced if not eliminated. The reduction in surface heating eliminates the adhesion of golf ball precursor products to one another prior to application of the cover 18. It

should further be appreciated that while the pre-heating is described as being after core formation, the present methods also contemplate heating the core 12 both during and after the formation of the golf ball core 12. In this manner, some of the heat that may be present or liberated in the core 12 from the core formation process may be used in the pre-heating of the core 12.

The thermal expansion of the golf ball precursor product results in the volume of the golf ball precursor product increasing from its initial size to a larger subsequent size. Preferably, the core 12 and boundary layer 14 are pre-heated, prior to applying the cover 18, to a temperature of about 120 °F to about 175 °F, and more preferably between about 140 °F to about 160 °F. If using convection heating, the pre-heating preferably occurs for about one hour, or for such time as needed to achieve an amount of thermal expansion prior to cover formation such that the cover will not crack, and/or to achieve a desired improvement in cover molding cycle time, as described below. If using microwave heating, the predetermined time period is much less than convection heating. Microwave heating of a 1.60 inch golf ball precursor product for two minutes at a power of 700 Watts in a 0.7 cubic foot microwave will thermally expand the golf ball precursor product by 0.001 inches. Although the duration of the pre-heating is not believed to be critical, the above-mentioned preferred amount of time permits substantially even heating of the core 12 and boundary layer 14, and results in substantially steady-state thermal conditions within the core 12 and boundary layer 14.

While the temperature ranges and heating times disclosed above are the preferred ranges and times, it should be noted that the invention is not limited to any exact temperature or heating time. The purpose of the pre-heating is to subject the core 12 and boundary layer 14 to an increase in temperature to result in volumetric thermal expansion of the golf ball precursor product. However, the temperature should be below the softening temperature of the materials of the golf ball precursor product. If a boundary layer 14 is utilized, the temperature is generally maintained below the softening temperature of the boundary layer 14. The expansion may occur within any number of absolute temperatures over any period of heating time that fall within the operability ranges of the materials used. For example, any temperature differential and heating time that causes a sufficient amount of thermal expansion of the golf ball precursor product may be used in practicing the present invention. The amount of thermal expansion preferred will vary depending on, at least, the cover material(s) and cover thickness to be used for manufacturing the golf ball 10. For example, for a relatively rigid cover material or a relatively thin cover, it is preferable to cause a relatively larger amount of thermal expansion to the golf ball precursor product to substantially prevent cover cracking.

The volumetric thermal expansion of the core 12 and boundary layer 14 may be expressed as a percentage, according to the following:

$$(1) \quad \left[\frac{\text{Vol}_{final} - \text{Vol}_{initial}}{\text{Vol}_{initial}} \times 100 \right] \%$$

where Vol_{final} is the average volume of the core 14 or the core 14 and one or more boundary layers 14 at the high temperature, and $Vol_{initial}$ is the average volume of the core 12 or the core 12 and one or more boundary layers 14 at the lower, initial starting temperature. It has been found that a volumetric expansion of at least about 1.2% is

5 substantially sufficient to prevent cover cracking when using a thermosetting polyurethane cover material in a casting process. It will be understood, however, that this is not intended to serve as a lower limit for the volumetric thermal expansion of the present methods. Instead, the lower limit of volumetric thermal expansion for a given system will depend on the materials, the golf ball construction (e.g., core diameter,

10 boundary layer and cover thickness, etc.), and the molding processes utilized in the system. Determination of this limit for a given system is within the level of skill of those skilled in the art.

After pre-heating, the golf ball precursor products may be stored in a hopper disposed in proximity to the cover molding apparatus. The golf ball precursor products

15 are then introduced to the cover molding apparatus for application of a cover 18 thereon. The cover 18 is preferably applied while the core 12 and optional boundary layer 14 are at an increased temperature, and most preferably at the increased temperature obtained during the pre-heating thereof. As described above, the cover 18 may be composed of one or more of several different types of materials, and may be

20 applied by any of several molding methods. In the preferred embodiment, the cover 18 is a thermosetting polyurethane that is applied in a cast molding process. As mentioned

previously, the curing of the polyurethane to form the cover is an exothermic reaction. After the cover 18 is applied to the golf ball precursor product, the golf ball 10 is further processed to form a finished ball.

The method for manufacturing golf balls described above provides numerous
5 benefits. One such benefit, as described above, is that by pre-heating the core 12 and boundary layer 14, the cracking of the cover 18 of the golf ball 10 is substantially minimized or avoided altogether. Also, by pre-heating the core 12 and boundary layer 14 before forming the cover 18 of the golf ball 10, the thermal expansion that would otherwise be present in the core 12 and boundary layer 14 due to the cover forming
10 process is reduced, as these components have already undergone thermal expansion. In addition, the pre-heating substantially prevents the core 12 and boundary layer 14 from acting as a heat sink that drains heat from the cover forming process. This may result in decreased cover molding cycle times of as much as about 30%. Moreover, the pre-heating of the core 12 and boundary layer 14 also facilitates the de-molding of the golf
15 ball 10 from a die.

EXAMPLES

The following examples demonstrate the efficacy of the present invention in preventing the cracking or fracturing of golf balls, especially multiple layer golf balls
20 having a thermosetting cover. Golf balls produced with a thermosetting polyurethane cover material, however unheated prior to application of the cover, exhibited cracking

at the seam of the golf ball. A determination was made that the exothermic reaction to form the thermosetting cover was the main cause of the cracking of the golf ball. Cores with boundary layers were produced and pre-heated prior to application of the cover.

The results of those experiments are shown in Examples One and Two.

5

EXAMPLE ONE

Golf ball precursor products consisting of a compression molded core composed of a polybutadiene-based material with an injection molded boundary layer composed of a blend of ionomers were measured cold, that is prior to pre-heating. The cores each had a diameter of 1.54 inches and a Rhiele compression of 82.5. The boundary layers
10 had a Shore D hardness of 65, and the diameter of the core and boundary layer was 1.63 inches. The measurements for Example One are provided in Table Four. The average diameter cold and the average volume cold are provided in Columns I and IV, respectively. The golf ball precursor products were convection heated for at least one hour at a temperature between 120 °F to about 175 °F. The average diameter hot and
15 the average volume hot were measured for the golf ball precursor products, and these measurements are provided in Columns II and V, respectively.

The percentage increase in diameter and volume for each golf ball precursor product is provided in Columns III and VI, respectively. A thermosetting polyurethane cover was applied to each of the golf ball precursor products subsequent to the pre-
20 heating. The weight, equatorial diameter and compression were measured for each of the covered golf balls and those results are provided in Columns VII, VIII and IX,

respectively. The covered golf balls of Example One, all of which were pre-heated prior to application of the cover, did not experience any cracking or fracturing of the cover.

Table Four

I	II	III	IV	V	VI	VII	VIII	IX
Avg. Diameter Cold (in)	Avg. Diameter Hot (in)	Avg. Diameter increase	Avg. Volume cold	Avg. Volume Hot	Avg. Volume increase	Weight with cover	Avg. size with cover	Compression with cover
1.644	1.654	0.64%	2.324	2.369	1.93%	46.216	1.681	107.5
1.632	1.642	0.61%	2.276	2.318	1.85%	46.338	1.685	103.0
1.644	1.654	0.61%	2.324	2.367	1.84%	46.087	1.681	107.5
1.634	1.644	0.61%	2.284	2.327	1.85%	46.162	1.682	107.5
1.633	1.641	0.49%	2.278	2.312	1.48%	46.278	1.681	109.0
1.634	1.641	0.43%	2.282	2.312	1.29%	46.342	1.684	103.5
1.635	1.646	0.70%	2.286	2.335	2.13%			
1.634	1.644	0.64%	2.282	2.327	1.94%	46.313	1.682	103.5
1.633	1.643	0.61%	2.280	2.322	1.85%	46.283	1.681	105.0
1.642	1.652	0.61%	2.316	2.358	1.84%	46.151	1.683	105.0
1.635	1.644	0.55%	2.289	2.327	1.66%	46.179	1.681	104.5
1.631	1.641	0.61%	2.270	2.312	1.85%	46.367	1.679	106.5
1.643	1.652	0.55%	2.320	2.358	1.65%	46.190	1.685	105.0
1.635	1.646	0.70%	2.286	2.335	2.13%	46.269	1.684	105.5
1.635	1.644	0.55%	2.286	2.324	1.66%	46.179	1.683	103.5
1.632	1.641	0.52%	2.276	2.312	1.57%	46.569	1.685	102.0
1.630	1.637	0.43%	2.265	2.295	1.29%	46.381	1.683	105.5
1.631	1.639	0.46%	2.272	2.303	1.39%	46.500	1.686	104.5

EXAMPLE TWO

Golf ball precursor products consisting of a compression molded core composed of a polybutadiene-based material with an injection molded boundary layer composed of a blend of ionomers were measured cold, that is prior to pre-heating. The cores each had a diameter of 1.52 inches and a Rhee compression of 79.35. The boundary layers each had a Shore D hardness of 67.5, and the diameter of the core and boundary layer

for each golf ball precursor product was 1.63 inches. The measurements for Example Two are provided in Table Five. The average diameter cold and the average volume cold are provided in Columns I and IV, respectively. The golf ball precursor products were convection heated for at least one hour at a temperature between 120 °F to about 5 175 °F. The average diameter hot and the average volume hot were measured for the golf ball precursor products, and these measurements are provided in Columns II and V, respectively. The percentage increase in diameter and volume for each golf ball precursor product is provided in Columns III and VI, respectively. A thermosetting polyurethane cover was applied to each of the golf ball precursor products subsequent 10 to the pre-heating. The weight, equatorial diameter and compression were measured for each of the covered golf balls and those results are provided in Columns VII, VIII and IX, respectively. The covered golf balls of Example One, all of which were pre-heated prior to application of the cover, did not experience any cracking or fracturing of the cover.

15

20

Table Five

				Avg. Diameter Cold (in)	Avg. Diameter Hot (in)	Avg. Diam. increase	Avg. Volume cold	Avg. Volume Hot	Avg. Volume increase	Weight with cover	Avg. size with cover	Compress. with cover
				1.631	1.644	0.80%	2.270	2.324	2.41%	46.507	1.685	108.5
2				1.630	1.641	0.64%	2.268	2.312	1.94%	46.506	1.682	110.0
3				1.631	1.642	0.67%	2.272	2.318	2.04%	46.603	1.680	108.0
4				1.630	1.640	0.61%	2.268	2.310	1.85%	46.544	1.683	109.5
5				1.632	1.643	0.67%	2.276	2.322	2.04%	46.628	1.677	113.5
6				1.631	1.641	0.61%	2.270	2.312	1.85%	46.501	1.680	108.0
7				1.630	1.639	0.58%	2.265	2.305	1.76%	46.573	1.678	108.5
8				1.632	1.641	0.52%	2.276	2.312	1.57%	46.640	1.679	109.5
9				1.629	1.640	0.64%	2.263	2.307	1.95%	46.574	1.677	108.0
10				1.631	1.643	0.74%	2.270	2.320	2.22%	46.568	1.678	107.5
11				1.628	1.638	0.61%	2.257	2.299	1.85%	46.537	1.678	109.0
12				1.628	1.640	0.74%	2.257	2.307	2.23%	46.484	1.683	106.5
13				1.632	1.643	0.64%	2.276	2.320	1.94%	46.655	1.681	110.5
14				1.630	1.641	0.68%	2.265	2.312	2.04%	46.458	1.682	111.0
15				1.631	1.642	0.67%	2.272	2.318	2.04%	46.504	1.682	105.0
16				1.632	1.643	0.64%	2.276	2.320	1.94%	46.599	1.679	110.5
17				1.631	1.641	0.64%	2.270	2.314	1.94%	46.505	1.680	109.5
18				1.630	1.640	0.58%	2.268	2.307	1.76%	46.621	1.683	110.5

CLAIMS

1. A golf ball comprising:
 - a core;
 - 5 a boundary layer covering the core, the boundary layer comprising a thermoplastic material having a Shore D hardness between 40 and 85;
 - a wound layer covering the boundary layer; and
 - a cover comprising a polyurethane material covering the wound layer.
- 10 2. The golf ball according to claim 1 wherein the polyurethane layer comprises a thermosetting polyurethane comprising a para-phenylene diisocyanate prepolymer.
3. The golf ball according to claim 1 wherein the polyurethane layer has a thickness in the range of 0.01 to 0.05 inches.
- 15 4. The golf ball according to claim 1 wherein the wound layer is wound to a thickness of between 0.080 and 0.100 inches.
5. The golf ball according to claim 1 wherein the boundary layer has a thickness of
- 20 0.03 to 0.10 inches.

6. The golf ball according to claim 1 wherein the boundary layer comprises a sodium neutralized ionomer, a zinc neutralized ionomer and a terpolymer.

5 7. The golf ball according to claim 1 wherein the core has a thickness between 1.30 inches and 1.55 inches.

8. The golf ball according to claim 1 wherein the core comprises a polybutadiene material and has a PGA compression of at least 55.

10

9. The golf ball according to claim 1 wherein the cover has a Shore D hardness less than 60 and the boundary layer has a Shore D hardness greater than 60.

10. The golf ball according to claim 1 wherein the wound layer has a tensile elastic
15 modulus of at least 10,000 pounds per square inch.

20

11. A method for forming a multiple-piece golf ball, the method comprising:
injection molding a boundary layer over a core, the boundary layer
comprising an thermoplastic material having a Shore D hardness in the range of 40 to
85;
5 winding a fiber around the boundary layer to form a wound layer; and
forming a polyurethane layer over the wound layer to form the four-
piece golf ball.
12. The method according to claim 11 wherein forming the polyurethane layer
10 comprises casting a thermosetting polyurethane layer over the wound layer.
13. The method according to claim 11 wherein forming the polyurethane layer
comprises injecting a thermoplastic polyurethane layer over the wound layer.
- 15 14. The method according to claim 11 further comprising compressing a cylinder of
a polybutadiene material to form a solid sphere core.
15. The method according to claim 11 further comprising coating the wound layer
in a latex solution prior to forming the polyurethane layer.

16. A golf ball comprising:

a solid core comprising a polybutadiene material, having a PGA compression of at least 55, and a diameter in the range of 1.35 inches to 1.58 inches;

a boundary layer covering the solid core, the boundary layer comprising
5 a blend of ionomer materials, having a Shore D hardness between 40 and 85 and a thickness in the range of 0.01 inches to 0.1 inches;

an optional wound layer covering the boundary layer, the wound layer having a thickness of 0.05 to 0.1 inches; and

a thermosetting polyurethane layer covering the boundary layer or the
10 optional wound layer, the thermosetting polyurethane layer having a thickness in the range of 0.01 inches to 0.05 inches.

17. A golf ball comprising:

a core with an optional boundary layer; and

15 a cover comprising a polyurethane material formed from reactants comprising a p-phenylene diisocyanate terminated polyester prepolymer in an amount up to 90 parts, a p-phenylene diisocyanate terminated polyether prepolymer in an amount up to 90 parts, 10 to 40 parts of a toluene diisocyanate polyurethane prepolymer.

18. The golf ball according to claim 17 wherein the polyurethane cover is formed from reactants comprising 20 parts of a p-phenylene diisocyanate terminated polyester prepolymer, 50 parts of a p-phenylene diisocyanate terminated polyether prepolymer, 30 parts of a toluene diisocyanate polyurethane prepolymer.

5

19. The golf ball according to claim 16 wherein the polyurethane cover is formed from reactants comprising 70 to 80 parts of a p-phenylene diisocyanate terminated polyether prepolymer, 20 to 30 parts of a toluene diisocyanate polyurethane prepolymer.

10

20. A golf ball comprising:

a core with an optional boundary layer and optional wound layer; and

a polyurethane cover formed from reactants comprising a toluene diisocyanate based polyurethane prepolymer, a second diisocyanate polyurethane prepolymer and at least one curing agent.

15

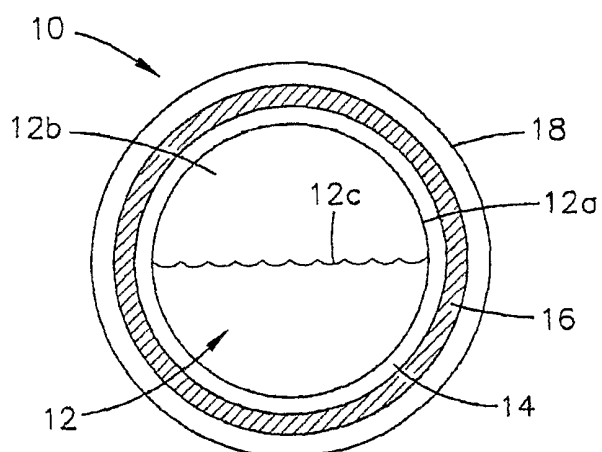
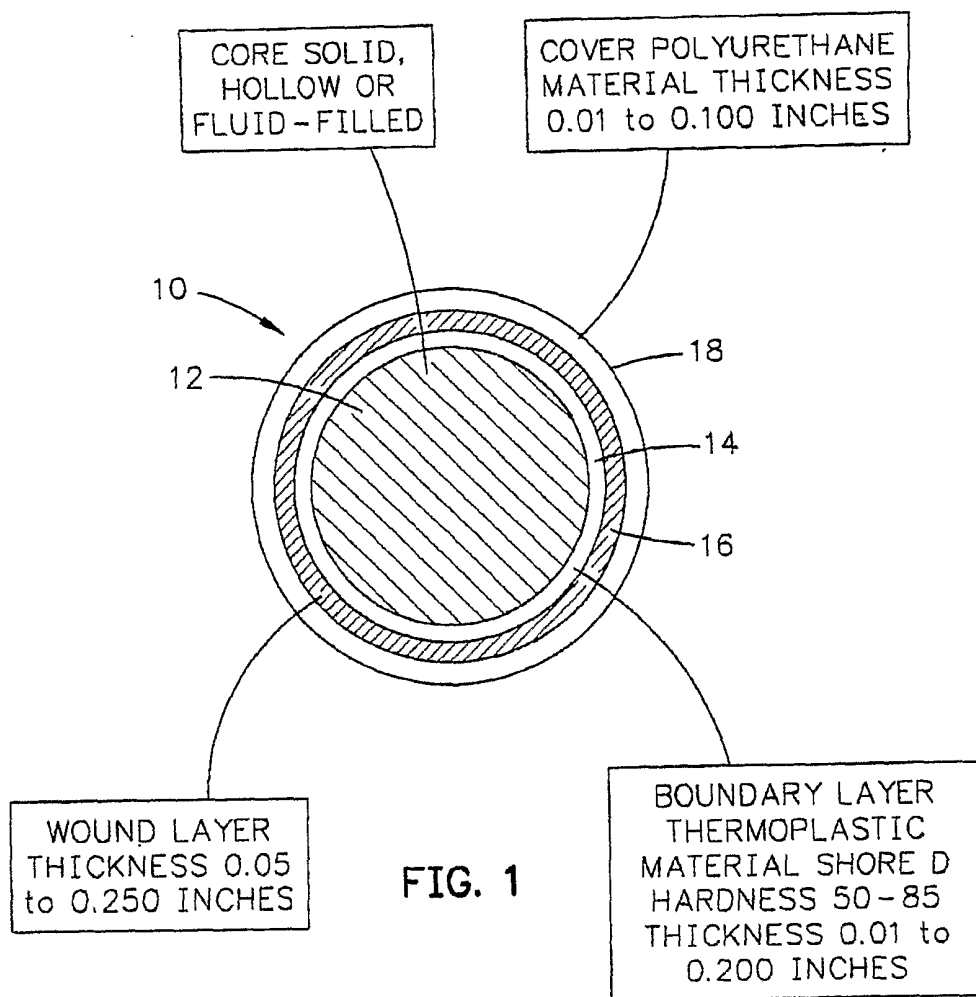
21. A golf ball comprising:

a core with an optional boundary layer and optional wound layer; and

a thermosetting polyurethane cover formed from reactants comprising a p-phenylene diisocyanate prepolymer and at least one curing agent.

20

22. A method of manufacturing a golf ball comprising:
- forming a core and an optional boundary layer surrounding the
- core;
- heating the core and the optional boundary layer such that the
- 5 core and the optional boundary layer undergo volumetric thermal expansion; and
- applying a cover over the thermally expanded core and the at least one
- boundary layer.
23. The method according to claim 22 wherein heating the core and the optional
- 10 boundary layer comprises convection heating the core and the optional boundary layer
- to a temperature within the range of about 120 °F to about 180 °F.
24. The method according to claim 22 wherein the cover is composed of an
- exothermic material.
- 15
25. The method according to claim 22 wherein the cover is composed of a
- thermosetting polyurethane material.



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/07132

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : A63B 37/06

US CL : 473/357

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 473/357, 356, 359, 360, 361, 362, 363, 364, 365

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,816,941 A (HAYASHI et al) 06 October 1998 (06.10.1998), See all.	1, 3-5, 7, 9, 11-14
---		-----
Y		6, 8, 10, 16
Y, P	US 6,117,024 A (DAWANJEE) 12 September 2000 (12.09.2000), See abstract.	2, 17, 20, 21
Y	US 4,272,079 A (NAKADE et al) 09 June 1981 (09.06.1981), See abstract.	15

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"

document member of the same patent family

Date of the actual completion of the international search

06 April 2001 (06.04.2001)

Date of mailing of the international search report

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