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(54) **RADIOLUMINESCENT GOLF BALL**

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ABSTRACT

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The invention is directed to a golf ball including a core and a cover, wherein at least one of the core or the cover includes a radioluminescent material; and, additionally, a golf ball including a core having a diameter of between about 1.5 and 1.59; a cover containing a radioluminescent powder, and a thermoplastic material. The radioluminescent powder is present in an amount sufficient to emanate light without activation with UV or visible light.

RADIOLUMINESCENT GOLF BALL

FIELD OF THE INVENTION

[0001] The present invention relates to golf balls and, more specifically, to golf balls employing an improved light emitting coating or composition.

BACKGROUND OF THE INVENTION

[0002] Along with the boom of the game of golf in recent years has come an increased demand for equipment and course resources. Whether due to novelty, necessity, or both, one arena that has become more popular is night golf. Many courses allow night play, host night golf tournaments, and even support night golf leagues. The golf balls used for night play are typically transparent to semi-transparent, one-piece balls, in which a hole is drilled to receive a light-generating device.

[0003] There are a number of processes by which light may be generated, most of which may be classified into a few categories, including triboluminescence, when light is emitted after the energy being absorbed is mechanical; bioluminescence, when light is emitted after the energy being absorbed is from a chemical reaction in a living organism (i.e., fireflies); chemiluminescence, when the light emitted after the energy being absorbed is from a chemical reaction (i.e., glow sticks); photoluminescence, when the light emitted after the energy being absorbed is from light; and thermoluminescence, when the light emitted after the energy being absorbed is from heat.

[0004] Because of the nature of the game of golf and the robustness required, the mechanism by which almost all night golf ball light devices operate, however, is chemiluminescence. Chemiluminescent devices are non-incandescent products which produce light from a mixture of chemicals. The production of light from a chemiluminescent device is conventionally based upon the reaction of a catalyzed hydrogen peroxide mixture (activator) with an oxalate. The activator reagent is typically contained within a breakable vial which, when broken, mixes with an oxalate reagent to produce the chemiluminescent light. The containment vessel is made of a clear or translucent material, such as polyethylene or polypropylene, that permits the light produced by the chemiluminescent device to pass through the vessel walls.

[0005] Chemiluminescent devices are commercially available in a variety of visible colors. A great variety of chemical reagents for producing light by chemiluminescent reaction are known, examples of which are disclosed in U.S. Pat. Nos. 5,043,851 and 5,508,893. The most familiar chemiluminescence products are the Cyalume® glow sticks, that emit green light originating from 9,10-bis(phenylethynyl)anthracene. The chemical 9,10-diphenylanthracene produces blue light.

[0006] However, the above-discussed lighting devices have many undesirable features, such as glass ampule breakage under violent movement. Once the glass ampules are broken, the solutions react with each other prematurely and cause the lighting ability of this device to be reduced greatly. Additionally, if the packaging is not completely light resistant or has been damaged, the lifetime of chemiluminescent products decreases dramatically.

[0007] Another problem that exists with current golf balls for night use is the golf ball itself. It is quite apparent that drilling a hole in the golf ball to receive a light-emitting device can damage the ball, limit the types of ball construction that can be used, or both. For example, the use of a wound construction is precluded because drilling a hole through the wound layer would destroy the integrity of the windings. Further, all materials of the golf ball must be transparent (or at least semi-transparent). This requirement severely limits the type of materials that may be used to form night golf balls.

[0008] There remains a need, therefore, for a light-generating process for golf balls that is robust, cheap, and efficient and yet allows construction of virtually any type of golf ball, from a one-piece ball to a dual core, double cover ball. Tritium, a radioactive isotope of hydrogen with an atomic mass of about 3, is commonly used to produce luminous watch dials and hands. The radioactivity is composed entirely of beta particles that are nearly completely absorbed by the watch crystal or glass covering the dial. The tritium used in watches today is in compliance with the international Standards ISO 3157 and NIHS 97-10, which define the acceptable minimum levels for the amount of luminescence required to see the watch dial in the dark. Depending on the quality of the radioluminescent compound, it can conserve its ability to luminescence for several years. The quality also influences the luminous intensity, which also depends on the surface and thickness of the deposit. The present invention describes the use of the energy release by tritium decay in golf ball coatings and compositions for an improved light-emitting golf ball.

SUMMARY OF THE INVENTION

[0009] The present invention is directed to a golf ball comprising a core and a cover, wherein at least one of the core or the cover comprises a radioluminescent material. The radioluminescent material includes tritium or a tritium-based material. Preferably, the cover includes the radioluminescent material. The radioluminescent material should be present in an amount sufficient to emanate light without activation by UV or visible light.

[0010] In one embodiment, the radioluminescent material is blended with a thermoplastic, thermoset, or thermoplastic elastomeric material. Additionally, the radioluminescent material further may be blended with polyurethanes, polyurethane-ureas, polyurea-urethanes, polyureas, polyurethane-ionomers, epoxies, silicones, and unsaturated polyesters.

[0011] While the ball construction can be any construction known to the skilled artisan, the core preferably includes a center and an outer core layer. In a preferred embodiment, the cover includes an inner cover layer and an outer cover layer. In an alternative embodiment, the core has a surface coated with the radioluminescent material and the cover is optically transparent.

[0012] The golf ball ideally has a coefficient of restitution of greater than about 0.78. In another embodiment, the cover has an outer surface comprising an indicia formed from the radioluminescent material.

[0013] The present invention is directed to a golf ball including a core and a cover, wherein the cover is coated

with a radioluminescent material. The radioluminescent material is present in an amount sufficient to emanate light without activation by UV or visible light. The cover coating may be in the form of a paint, an ink, a paste, a clearcoat, a primer, or a mixture thereof. In one embodiment, the cover coating is further coated with a clearcoat for protection.

[0014] The core may be formed of a center and an outer core layer and, in one embodiment, the cover may include an inner cover layer and an outer cover layer. Ideally, the golf ball has a coefficient of restitution of greater than about 0.78.

[0015] The present invention is also directed to a golf ball comprising a core and a cover, wherein the core has a diameter of between about 1.5 and 1.59; the cover comprises a radioluminescent powder and a thermoplastic material; and the golf ball has a coefficient of restitution of greater than about 0.78; and wherein the radioluminescent powder is present in an amount sufficient to emanate light without activation with UV or visible light.

DETAILED DESCRIPTION OF THE INVENTION

[0016] The golf balls of the present invention may comprise any of a variety of constructions, from a simple one-piece solid ball, to a two-piece ball formed of a core and cover, to a three piece dual core single cover to any multi-piece construction, but preferably include a core formed of a center and at least one outer core layer and a cover formed of an outer cover layer and at least one inner cover layer. The core and/or the cover layers may be formed of more than one layer and an intermediate or mantle layer may be disposed between the core and the cover of the golf ball. The innermost portion of the core, while preferably solid, may be a hollow or a liquid-, gel-, or air-filled sphere. As with the core, the cover layers may also comprise a plurality of layers, at least one of which may be an adhesive or coupling layer. The layers may be continuous or non-continuous (i.e., grid-like). The core may also comprise a solid or liquid filled center around which many yards of a tensioned elastomeric material are wound.

[0017] The light-generating tritium decay of the present invention may be associated with any component of the golf ball but is preferably in the cover, either blended with the cover material or as a coating over the cover. It is also envisioned that the tritium decay light emission may emanate from the inner cover or outer core materials, or a coating thereon, in association with an optically-transparent outer cover layer.

[0018] Once inside the cover materials, blends, or coatings, the radioluminescent materials would pose no health threat for golfers. The amount of tritium used to provide the luminescence that enables the golf balls to be seen in the dark is quite low and poses no health risk. Tritium is a pure beta emitter, decaying to helium with a half life of about 12 years. The roughly 18 keV beta particles can be stopped by a piece of paper and is not hazardous. Not only is the level of radioactivity quite low, but because tritium emits a very low energy beta particle, it is retained within the material and never reaches the golfer or the surrounding environment. Tritium powder for the present invention may be obtained commercially from RC TRITEC® AG of Teufen, Switzerland.

[0019] A variety of methods may be used to load the cover or coating materials with tritium. These include: 1) catalytic exchange with tritium gas, in which hydrogen atoms, preferably in aromatic positions, are randomly exchanged with tritium allowing the target molecule to be labeled directly without prior preparation of a precursor compound; 2) catalytic reduction with tritium gas, in which unsaturated organic compounds are reduced with appropriate catalysts; 3) catalytic dehalogenation with tritium gas, in which bromine and iodine atoms are exchanged with tritium in catalytic reactions; and 4) reduction with metal tritides, in which complex organic molecules with several functional groups can require soft and specific tritide reactants.

[0020] Tritium-activated radioluminescent compounds or paints allow permanent emission over a long period of time without prior activation (i.e., activation by exposure to UV or light). The energy release of the tritium decay is continuously converted into a weak light emission. Traces of a solid, tritiated polymer may be coated on the golf balls, blended with golf ball component materials, or coated on zinc sulphide crystals that are blended with the component materials, to act as a permanent energy source. Tritium-activated radioluminescent compounds are available in many luminosity classes (2.5-160 $\mu\text{Cd/g}$) and a variety of ISO colors. While any emission color is suitable for the present invention, preferred colors include white; yellow; greenish-yellow; green; blue-green; and a wide variety specific colors, even PANTONE® colors, including yellow; orange; red; green; and blue.

[0021] Additionally, tritium-based powder materials may be subsequently mixed with specially adapted transparent binders. The resulting paste is applied by suitable tooling to various golf ball components and, in particular, covers or cover coatings.

[0022] In another embodiment, the golf balls of the present invention include the Super-LumiNova® pigments from RC TRITEC® AG, also called photo-luminescent or afterglow pigments. These are non-radioactive alternatives for the golf balls of the present invention. These chemical compositions provide up to 100 times higher brightness than the above-described zinc sulphide type materials. After sufficient activation by sunlight or artificial light, these pigments glow in the dark for many hours. The activation and subsequent light emission process can be repeated and the materials are extremely resistant to aging.

[0023] All of the above-mentioned luminous pigments are preferably used as dry powder and are mixed for processing with highly transparent binders, commercially-available from RC TRITEC®. The binders have characteristics that include, but are not limited to being UV curable; have a mat and/or glossy appearance; have excellent brightness yield; protect against discoloration; have excellent adhesion on various substrates; are easily processed, and are highly luminescing. Additionally, tritium self-luminous paints and Super-LumiNova® high performance phosphorescent paints, in various grades and colors, are suitable for application to various golf ball components of the present invention.

[0024] The radioluminescent of the present invention may be present in outer core layers, inner and outer cover layers, and coatings, which include coatings applied over the core (i.e., solid, wound, hollow, foam, liquid, or gel), and/or over

a core layer, cover layer, or conventional top-coat. If used in a coating, preferably, the radioluminescent materials are incorporated into one or more layers of a primer, clearcoat, or top-coat.

[0025] If the radioluminescent materials are used in a core layer, preferably covered by a transparent or semi-transparent cover (or translucent), they may be alone or in blends with conventional polybutadiene rubber thermoset materials as a single or dual core, as well as blends with many conventional thermoplastic or thermoset materials in a multi-piece core.

[0026] A preferred use of the radioluminescent materials of the present invention are blends with polyurethanes, polyurethane-ureas, polyurea-urethanes, polyureas, polyurethane-ionomers, epoxies, silicones, and unsaturated polyesters as inner or outer cover materials. These layers may be formed in a variety of methods, however preferably they are applied (i.e., sprayed, dipped, etc.) or molded using reaction injection molding, casting, laminating, or otherwise forming a thermoplastic or preferably thermoset layer of polymer from liquid reactive components.

[0027] The radioluminescent materials may also be blended with thermoplastic composites wherein the thermoplastic materials comprise ionomers, polyurethanes, polyurethane-ureas, polyurea-urethanes, polyureas, metalocenes (including grafted metalocenes), polyamides, PEBAX®, HYTREL®, and other suitable materials, such as those described in U.S. Pat. Nos. 6,149,535 and 6,152,834, which are incorporated herein, in their entirety, by express reference thereto.

[0028] Suitable polyurethane-type materials for blending with the radioluminescent materials of the present invention or which by any cover layer, preferably outer cover layers may be formed if not blended with the luminescent and/or phosphorescent materials include, but are not limited to, polyurethanes, polyurethane-ureas, polyurea-urethanes, polyureas, or epoxies, that generally comprise the reaction product of at least one polyisocyanate, polyol, and at least one curing agent. Any polyisocyanate available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyisocyanates include, but are not limited to, 4,4'-diphenylmethane diisocyanate ("MDI"); polymeric MDI; carbodiimide-modified liquid MDI; 4,4'-dicyclohexylmethane diisocyanate ("H₁₂MDI"); p-phenylene diisocyanate ("PPDI"); m-phenylene diisocyanate ("MPDI"); toluene diisocyanate ("TDI"); 3,3'-dimethyl-4,4'-biphenylene diisocyanate ("TODI"); isophoronediiisocyanate ("IPDI"); hexamethylene diisocyanate ("HDI"); naphthalene diisocyanate ("NDI"); xylene diisocyanate ("XDI"); p-tetramethylxylene diisocyanate ("TMXDI"); m-tetramethylxylene diisocyanate ("TMXDI"); ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; cyclohexyl diisocyanate; 1,6-hexamethylene-diisocyanate; dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,4,4-trimethyl-1,6-hexane diisocyanate ("TMDI"); tetracene diisocyanate; naphthalene diisocyanate; anthracene diisocyanate; isocyanurate of toluene diisocyanate; uretdione of hexamethylene diisocyanate; and mixtures thereof. Prefer-

ably, the polyisocyanate includes MDI, PPDI, TDI, or a mixture thereof. It should be understood that, as used herein, the term "MDI" includes 4,4'-diphenylmethane diisocyanate, polymeric MDI, carbodiimide-modified liquid MDI, and mixtures thereof and, additionally, that the diisocyanate employed may be "low free monomer," understood by one of ordinary skill in the art to have lower levels of "free" monomer isocyanate groups, typically less than about 0.1% free monomer groups. Examples of "low free monomer" diisocyanate include, but are not limited to Low Free Monomer MDI, Low Free Monomer TDI, Low Free Monomer HDI, and Low Free Monomer PPDI.

[0029] The polyisocyanate should have less than about 14% unreacted NCO groups. Preferably, the at least one polyisocyanate has no greater than about 7.5% NCO, and more preferably, less than about 7.0%. It is well understood in the art that the hardness of polyurethane can be correlated to the percent of unreacted NCO groups.

[0030] Any polyol available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyols include, but are not limited to, polyether polyols, hydroxy-terminated polybutadiene (including partially/fully hydrogenated derivatives), polyester polyols, polycaprolactone polyols, and polycarbonate polyols. In one preferred embodiment, the polyol includes a polyether polyol, such as polytetramethylene ether glycol ("PTMEG"), polyethylene propylene glycol, polyoxypropylene glycol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds and substituted or unsubstituted aromatic and cyclic groups. Preferably, the polyol of the present invention includes PTMEG.

[0031] Suitable polyester polyols include, but are not limited to, polyethylene adipate glycol; polybutylene adipate glycol; polyethylene propylene adipate glycol; o-phthalate-1,6-hexanediol; poly(hexamethylene adipate)glycol; and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups. Suitable polycaprolactone polyols include, but are not limited to, 1,6-hexanediol-initiated polycaprolactone, diethylene glycol initiated polycaprolactone, trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, PTMEG-initiated polycaprolactone, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

[0032] Suitable polycarbonates include, but are not limited to, polyphthalate carbonate and poly(hexamethylene carbonate)glycol. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

[0033] Polyamine curatives are also suitable for use in polyurethane covers. Preferred polyamine curatives include, but are not limited to, 3,5-dimethylthio-2,4-toluenediamine and isomers thereof; 3,5-diethyltoluene-2,4-diamine and isomers thereof, such as 3,5-diethyltoluene-2,6-diamine; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline) ("MCDEA"); polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkyldiamino diphenyl methane; p,p'-methylene dianiline ("MDA"); m-phenylenediamine ("MPDA");

4,4'-methylene-bis-(2-chloroaniline) ("MOCA"); 4,4'-methylene-bis-(2,6-diethylaniline) ("MDEA"); 4,4'-methylene-bis-(2,3-dichloroaniline) ("MDCA"); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenylmethane; trimethylene glycol di-p-aminobenzoate; and mixtures thereof. Preferably, the curing agent of the present invention includes 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, such as ETHACURE® 300, commercially available from Albermarle Corporation of Baton Rouge, La. Suitable polyamine curatives include both primary and secondary amines.

[0034] At least one of a diol, triol, tetraol, or hydroxy-terminated curatives may be added to the aforementioned polyurethane composition. Suitable diol, triol, and tetraol groups include ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy) benzene; 1,3-bis-[2-(2-hydroxyethoxy) ethoxy]benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(β -hydroxyethyl)ether; hydroquinone-di-(β -hydroxyethyl)ether; and mixtures thereof. Preferred hydroxy-terminated curatives include 1,3-bis(2-hydroxyethoxy)benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene; 1,4-butanediol, and mixtures thereof.

[0035] Both the hydroxy-terminated and amine curatives can include one or more saturated, unsaturated, aromatic, and cyclic groups. Additionally, the hydroxy-terminated and amine curatives can include one or more halogen groups. The polyurethane composition can be formed with a blend or mixture of curing agents. If desired, however, the polyurethane composition may be formed with a single curing agent.

[0036] In a particularly preferred embodiment of the present invention, saturated (aliphatic) polyurethanes are used to form cover layers, preferably outer cover layers and are blended with the luminescent and/or phosphorescent materials. The thermoset polyurethanes may be castable, reaction injection moldable, sprayable, or applied in a laminate form or by any technical known in the art. The thermoplastic polyurethanes may be processed using any number of compression or injection techniques. In one embodiment, the saturated polyurethanes are substantially free of aromatic groups or moieties.

[0037] Saturated diisocyanates which can be used include, but are not limited to, ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene-diisocyanate; 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; dicyclohexylmethane diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isophorone diisocyanate ("IPDI"); methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate ("TMDI"). The most preferred saturated diisocyanates are 4,4'-dicyclohexylmethane diisocyanate and isophorone diisocyanate ("IPDI").

[0038] Saturated polyols which are appropriate for use in this invention include, but are not limited to, polyether polyols such as polytetramethylene ether glycol and poly-

(oxypropylene)glycol. Suitable saturated polyester polyols include polyethylene adipate glycol, polyethylene propylene adipate glycol, polybutylene adipate glycol, polycarbonate polyol and ethylene oxide-capped polyoxypropylene diols. Saturated polycaprolactone polyols which are useful in the invention include diethylene glycol initiated polycaprolactone, 1,4-butanediol initiated polycaprolactone, 1,6-hexanediol initiated polycaprolactone; trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, PTMEG-initiated polycaprolactone. The most preferred saturated polyols are PTMEG and PTMEG-initiated polycaprolactone.

[0039] Suitable saturated curatives include 1,4-butanediol, ethylene glycol, diethylene glycol, polytetramethylene ether glycol, propylene glycol; trimethanolpropane; tetra-(2-hydroxypropyl)-ethylenediamine; isomers and mixtures of isomers of cyclohexyldimethylol, isomers and mixtures of isomers of cyclohexane bis(methylamine); triisopropanolamine, ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, 4,4'-dicyclohexylmethane diamine, 2,2,4-trimethyl-1,6-hexanediolamine; 2,4,4-trimethyl-1,6-hexanediolamine; diethyleneglycol di-(aminopropyl)ether; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,2-bis-(sec-butylamino)cyclohexane; 1,4-bis-(sec-butylamino)cyclohexane; isophorone diamine, hexamethylene diamine, propylene diamine, 1-methyl-2,4-cyclohexyl diamine, 1-methyl-2,6-cyclohexyl diamine, 1,3-diaminopropane, dimethylamino propylamine, diethylamino propylamine, imido-bis-propylamine, isomers and mixtures of isomers of diaminocyclohexane, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, and diisopropanolamine. The most preferred saturated curatives are 1,4-butanediol, 1,4-cyclohexyldimethylol and 4,4'-bis-(sec-butylamino)-dicyclohexylmethane.

[0040] Suitable catalysts include, but are not limited to bismuth catalyst, oleic acid, triethylenediamine (DABCO®-33LV), di-butyltin dilaurate (DABCO®-T12) and acetic acid. The most preferred catalyst is di-butyltin dilaurate (DABCO®-T12). DABCO® materials are manufactured by Air Products and Chemicals, Inc.

[0041] It is well known in the art that if the saturated polyurethane materials are to be blended with other thermoplastics, care must be taken in the formulation process so as to produce an end product which is thermoplastic in nature. Thermoplastic materials may be blended with other thermoplastic materials, but thermosetting materials are difficult if not impossible to blend homogeneously after the thermosetting materials are formed. Preferably, the saturated polyurethane comprises from about 1 to about 100%, more preferably from about 10 to about 75% of the cover composition and/or the intermediate layer composition. About 90 to about 10%, more preferably from about 90 to about 25% of the cover and/or the intermediate layer composition is comprised of one or more other polymers and/or other materials as described below. Such polymers include, but are not limited to polyurethane/polyurea ionomers, polyurethanes or polyureas, epoxy resins, polyethylenes, polyamides and polyesters, polycarbonates and polyacrylin. Unless otherwise stated herein, all percentages are given in percent by weight of the total composition of the golf ball layer in question.

[0042] Polyurethane prepolymers are produced by combining at least one polyol, such as a polyether, polycaprolactone, polycarbonate or a polyester, and at least one isocyanate. Thermosetting polyurethanes are obtained by curing at least one polyurethane prepolymer with a curing agent selected from a polyamine, triol or tetraol. Thermoplastic polyurethanes are obtained by curing at least one polyurethane prepolymer with a diol curing agent. The choice of the curatives is critical because some urethane elastomers that are cured with a diol and/or blends of diols do not produce urethane elastomers with the impact resistance required in a golf ball cover. Blending the polyamine curatives with diol cured urethane elastomeric formulations leads to the production of thermoset urethanes with improved impact and cut resistance. Other suitable thermoplastic polyurethane resins include those disclosed in U.S. Pat. No. 6,235,830, which is incorporated herein, in its entirety, by express reference thereto.

[0043] The golf ball layers may or may not include the radioluminescent materials of the present invention and can be one or more (a blend) homopolymeric or copolymeric materials, such as:

[0044] (1) Vinyl resins, such as those formed by the polymerization of vinyl chloride, or by the copolymerization of vinyl chloride with vinyl acetate, acrylic esters or vinylidene chloride;

[0045] (2) Polyolefins, such as polyethylene, polypropylene, polybutylene and copolymers such as ethylene methylacrylate, ethylene ethylacrylate, ethylene vinyl acetate, ethylene methacrylic or ethylene acrylic acid or propylene acrylic acid and copolymers and homopolymers produced using a single-site catalyst or a metallocene catalyst;

[0046] (3) Polyurethanes, such as those prepared from polyols and diisocyanates or polyisocyanates and those disclosed in U.S. Pat. No. 5,334,673;

[0047] (4) Polyureas, such as those disclosed in U.S. Pat. No. 5,484,870;

[0048] (5) Polyamides, such as poly(hexamethylene adipamide) and others prepared from diamines and dibasic acids, as well as those from amino acids such as poly(caprolactam), and blends of polyamides with SURLYN®, polyethylene, ethylene copolymers, ethyl-propylene-non-conjugated diene terpolymer, and the like;

[0049] (6) Acrylic resins and blends of these resins with poly vinyl chloride, elastomers, and the like;

[0050] (7) Thermoplastics, such as urethanes; olefinic thermoplastic rubbers, such as blends of polyolefins with ethylene-propylene-non-conjugated diene terpolymer; block copolymers of styrene and butadiene, isoprene or ethylene-butylene rubber; or copoly-(ether-amide), such as PEBAX®, sold by ELF Atochem of Philadelphia, Pa.;

[0051] (8) Polyphenylene oxide resins or blends of polyphenylene oxide with high impact polystyrene as sold under the trademark NORYL® by General Electric Company of Pittsfield, Mass.;

[0052] (9) Thermoplastic polyesters, such as polyethylene terephthalate, polybutylene terephthalate,

polyethylene terephthalate/glycol modified and elastomers sold under the trademarks HYTREL® by E.I. DuPont de Nemours & Co. of Wilmington, Del., and LOMOD® by General Electric Company of Pittsfield, Mass.;

[0053] (10) Blends and alloys, including polycarbonate with acrylonitrile butadiene styrene, polybutylene terephthalate, polyethylene terephthalate, styrene maleic anhydride, polyethylene, elastomers, and the like, and polyvinyl chloride with acrylonitrile butadiene styrene or ethylene vinyl acetate or other elastomers; and

[0054] (11) Blends of thermoplastic rubbers with polyethylene, propylene, polyacetal, nylon, polyesters, cellulose esters, and the like.

[0055] Any of the cover layers, which may or may not contain the radioluminescent materials of the present invention, can include polymers, such as ethylene, propylene, butene-1 or hexane-1 based homopolymers or copolymers including functional monomers, such as acrylic and methacrylic acid and fully or partially neutralized ionomer resins 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), acrylonitrile-butadiene, acrylic-styrene-acrylonitrile, poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene vinyl alcohol), poly(tetrafluoroethylene) and their copolymers including functional co-monomers, and blends thereof. Suitable cover compositions also include a polyether or polyester thermoplastic urethane, a thermoset polyurethane, a low modulus ionomer, such as acid-containing ethylene copolymer ionomers, including E/X/Y terpolymers where E is ethylene, X is an acrylate or methacrylate-based softening comonomer present in about 0 to 50 weight percent and Y is acrylic or methacrylic acid present in about 5 to 35 weight percent. Preferably, the acrylic or methacrylic acid is present in about 8 to 35 weight percent, more preferably 8 to 25 weight percent, and most preferably 8 to 20 weight percent.

[0056] Any of the inner or outer cover layers may also be formed from polymers containing α,β -unsaturated carboxylic acid groups, or the salts thereof, that have been 100 percent neutralized by organic fatty acids. The acid moieties of the highly-neutralized polymers ("HNP"), typically ethylene-based ionomers, are preferably neutralized greater than about 70%, more preferably greater than about 90%, and most preferably at least about 100%. The HNP's can be also be blended with a second polymer component, which, if containing an acid group, may be neutralized in a conventional manner, by the organic fatty acids of the present invention, or both.

[0057] The second polymer component, which may be partially or fully neutralized, preferably comprises ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, polyamides, polycarbonates, polyesters, polyurethanes, polyureas, thermoplastic elastomers, polybutadiene rubber, balata, metallocene-catalyzed polymers (grafted and non-grafted), single-site polymers, high-crystalline acid polymers, cationic ionomers, and the like.

[0058] The acid copolymers can be described as E/X/Y copolymers where E is ethylene, X is an α,β -ethylenically

unsaturated carboxylic acid, and Y is a softening comonomer. In a preferred embodiment, X is acrylic or methacrylic acid and Y is a C₁₋₈ alkyl acrylate or methacrylate ester. X is preferably present in an amount from about 1 to about 35 weight percent of the polymer, more preferably from about 5 to about 30 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer. Y is preferably present in an amount from about 0 to about 50 weight percent of the polymer, more preferably from about 5 to about 25 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer.

[0059] The organic acids are aliphatic, mono-functional (saturated, unsaturated, or multi-unsaturated) organic acids. Salts of these organic acids may also be employed. The salts of organic acids of the present invention include the salts of barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, or calcium, salts of fatty acids, particularly stearic, bebenic, erucic, oleic, linoelic or dimerized derivatives thereof. It is preferred that the organic acids and salts of the present invention be relatively non-migratory (they do not bloom to the surface of the polymer under ambient temperatures) and non-volatile (they do not volatilize at temperatures required for melt-blending).

[0060] Thermoplastic polymer components, such as copolyetheresters, copolyesteresters, copolyetheramides, elastomeric polyolefins, styrene diene block copolymers and their hydrogenated derivatives, copolyesteramides, thermoplastic polyurethanes, such as copolyetherurethanes, copolyesterurethanes, copolyureaurethanes, epoxy-based polyurethanes, polycaprolactone-based polyurethanes, polyureas, and polycarbonate-based polyurethanes fillers, and other ingredients, if included, can be blended in either before, during, or after the acid moieties are neutralized.

[0061] A variety of conventional components can be added to these cover compositions. These include, but are not limited to, white pigment such as TiO₂, ZnO, optical brighteners, surfactants, processing aids, foaming agents, density-controlling fillers, UV stabilizers and light stabilizers. Saturated polyurethanes are resistant to discoloration. However, they are not immune to deterioration in their mechanical properties upon weathering. Addition of UV absorbers and light stabilizers to any of the above compositions and, in particular, the polyurethane or polyurea compositions, help to maintain the tensile strength, elongation, and color stability. Suitable UV absorbers and light stabilizers include TINUVIN® 328, TINUVIN® 213, TINUVIN® 765, TINUVIN® 770 and TINUVIN® 622. The preferred UV absorber is TINUVIN® 328, and the preferred light stabilizer is TINUVIN® 765. TINUVIN® products are available from Ciba-Geigy. Dyes, as well as optical brighteners and fluorescent pigments may also be included in the golf ball covers produced with polymers formed according to the present invention. Such additional ingredients may be added in any amounts that will achieve their desired purpose.

[0062] Any method known to one of ordinary skill in the art may be used to synthesize the polyurethane or polyurea materials. One commonly employed method, known in the art as a one-shot method, involves concurrent mixing of the

polyisocyanate, polyol, and curing agent. This method results in a mixture that is inhomogenous (more random) and affords the manufacturer less control over the molecular structure of the resultant composition. A preferred method of mixing is known as a prepolymer method. In this method, the polyisocyanate and the polyol are mixed separately prior to addition of the curing agent. This method affords a more homogeneous mixture resulting in a more consistent polymer composition.

[0063] Other methods suitable for forming the layers and, in particular, those containing the radioluminescent materials of the present invention, include reaction injection molding, liquid injection molding, and pre-reacting the components to form an injection moldable thermoplastic polyurethane and then injection molding, all of which are known to one of ordinary skill in the art.

[0064] It has been found by the present invention that the use of a castable, reactive material, which is applied in a fluid form, makes it possible to obtain very thin outer cover layers on golf balls. Specifically, it has been found that castable, reactive liquids, which react to form a urethane elastomer material, provide desirable very thin outer cover layers.

[0065] The castable, reactive liquid employed to form the urethane elastomer material can be applied over the core using a variety of application techniques such as spraying, dipping, spin coating, or flow coating methods which are well known in the art. An example of a suitable coating technique is that which is disclosed in U.S. Pat. No. 5,733, 428, the disclosure of which is hereby incorporated by reference in its entirety in the present application.

[0066] The outer covers are preferably formed around the inner cover by mixing and introducing the material in the mold halves. The luminescent and/or phosphorescent materials may be added at any time in the process. It is important that the viscosity be measured over time, so that the subsequent steps of filling each mold half, introducing the core into one half and closing the mold can be properly timed for accomplishing centering of the core cover halves fusion and achieving overall uniformity. Suitable viscosity range of the curing urethane mix for introducing cores into the mold halves is determined to be approximately between about 2,000 cP and about 30,000 cP, with the preferred range of about 8,000 cP to about 15,000 cP.

[0067] To start the cover formation, mixing of the prepolymer and curative is accomplished in motorized mixer including mixing head by feeding through lines metered amounts of curative and prepolymer. Top preheated mold halves are filled and placed in fixture units using centering pins moving into holes in each mold. At a later time, a bottom mold half or a series of bottom mold halves have similar mixture amounts introduced into the cavity. After the reacting materials have resided in top mold halves for about 40 to about 80 seconds, a core is lowered at a controlled speed into the gelling reacting mixture.

[0068] A ball cup holds the ball core through reduced pressure (or partial vacuum). Upon location of the coated core in the halves of the mold after gelling for about 40 to about 80 seconds, the vacuum is released allowing core to be released. The mold halves, with core and solidified cover half thereon, are removed from the centering fixture unit,

inverted and mated with other mold halves which, at an appropriate time earlier, have had a selected quantity of reacting polyurethane prepolymer and curing agent introduced therein to commence gelling.

[0069] Similarly, U.S. Pat. No. 5,006,297 and U.S. Pat. No. 5,334,673 both also disclose suitable molding techniques which may be utilized to apply the castable reactive liquids employed in the present invention. Further, U.S. Pat. Nos. 6,180,040 and 6,180,722 disclose methods of preparing dual core golf balls. The disclosures of these patents are hereby incorporated by reference in their entirety. However, the method of the invention is not limited to the use of these techniques.

[0070] The resultant golf balls typically have a coefficient of restitution of greater than about 0.7, preferably greater than about 0.75, more preferably greater than about 0.78, and most preferably greater than about 0.800. The golf balls also typically have an Atti compression of at least about 30, preferably from about 50 to 120, and more preferably from about 60 to 100. A golf ball core layer, i.e., either the innermost core or any enclosing core layer, typically has a hardness of at least about 20 Shore A, preferably between about 20 Shore A and 80 Shore D, more preferably between about 30 Shore A and 65 Shore D.

[0071] When golf balls are prepared according to the invention, they typically will have dimple coverage greater than about 60 percent, preferably greater than about 65 percent, and more preferably greater than about 75 percent. The flexural modulus of the cover on the golf balls, as measured by ASTM method D6272-98, Procedure B, is typically greater than about 100 psi, and is preferably from about 500 psi to 150,000 psi. As discussed herein, the outer cover layer is preferably formed from a relatively soft polyurethane material. In particular, the material of the outer cover layer should have a material hardness, as measured by ASTM-D2240, less than about 70 Shore D, more preferably between about 25 and about 50 Shore D, and most preferably between about 40 and about 48 Shore D. The inner cover layer preferably has a material hardness of less than about 70 Shore D, more preferably between about 20 and about 70 Shore D, and most preferably, between about 25 and about 65 Shore D.

[0072] The core of the present invention has an Atti compression of less than about 120, more preferably, between about 20 and about 100, and most preferably, between about 40 and about 80. In an alternative, low compression embodiment, the core has an Atti compression less than about 20.

[0073] The overall outer diameter of the core is less than about 1.650 inches, preferably, no greater than 1.620 inches, more preferably between about 1.500 inches and about 1.610 inches, and most preferably between about 1.52 inches to about 1.60 inches. The outer diameter of the inner cover layer is preferably between 1.580 inches and about 1.650 inches, more preferably between about 1.590 inches to about 1.630 inches, and most preferably between about 1.600 inches to about 1.630 inches.

[0074] The present multi-layer golf ball can have an overall diameter of any size. Although the United States Golf Association specifications limit the minimum size of a competition golf ball to 1.680 inches. There is no speci-

cation as to the maximum diameter. Golf balls of any size, however, can be used for recreational play. The preferred diameter of the present golf balls is from about 1.680 inches to about 1.800 inches. The more preferred diameter is from about 1.680 inches to about 1.760 inches. The most preferred diameter is about 1.680 inches to about 1.740 inches.

[0075] It should be understood, especially to one of ordinary skill in the art, that there is a fundamental difference between "material hardness" and "hardness, as measured directly on a golf ball." Material hardness is defined by the procedure set forth in ASTM-D2240 and generally involves measuring the hardness of a flat "slab" or "button" formed of the material of which the hardness is to be measured. Hardness, when measured directly on a golf ball (or other spherical surface) is a completely different measurement and, therefore, results in a different hardness value. This difference results from a number of factors including, but not limited to, ball construction (i.e., core type, number of core and/or cover layers, etc.), ball (or sphere) diameter, and the material composition of adjacent layers. It should also be understood that the two measurement techniques are not linearly related and, therefore, one hardness value cannot easily be correlated to the other.

[0076] The radioluminescent materials of the present invention may also be used in golf equipment, in particular, inserts for golf clubs, such as putters, irons, and woods, and in golf shoes and components thereof. Further, the radioluminescent materials of the present invention may be used in indicia on the surface of the golf ball cores or covers. For example, it is envisioned that the Titleist® "script" or the golf ball number may be formed of a pigment, ink, or dye containing the radioluminescent material, powder, or paste.

[0077] As used herein, the term "about," used in connection with one or more numbers or numerical ranges, should be understood to refer to all such numbers, including all numbers in a range.

[0078] The invention described and claimed herein is not to be limited in scope by the specific embodiments herein disclosed, since these embodiments are intended as illustrations of several aspects of the invention. Any equivalent embodiments are intended to be within the scope of this invention. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

What is claimed is:

1. A golf ball comprising a core and a cover, wherein at least one of the core or the cover comprises a radioluminescent material.
2. The golf ball of claim 1, wherein the radioluminescent material comprises tritium or a tritium-based material.
3. The golf ball of claim 1, wherein the cover comprises the radioluminescent material.
4. The golf ball of claim 1, wherein the radioluminescent material is present in an amount sufficient to emanate light without activation by UV or visible light.
5. The golf ball of claim 1, wherein the radioluminescent material is blended with a thermoplastic, thermoset, or thermoplastic elastomeric material.
6. The golf ball of claim 1, wherein the radioluminescent material further comprises polyurethanes, polyurethane-

ureas, polyurea-urethanes, polyureas, polyurethane-ionomers, epoxies, silicones, and unsaturated polyesters.

7. The golf ball of claim 1, wherein the core comprises a center and an outer core layer.

8. The golf ball of claim 1, wherein the cover comprises an inner cover layer and an outer cover layer.

9. The golf ball of claim 1, wherein the core has a surface coated with the radioluminescent material.

10. The golf ball of claim 9, wherein the cover is optically transparent.

11. The golf ball of claim 1, wherein the golf ball has a coefficient of restitution of greater than about 0.78.

12. The golf ball of claim 1, wherein the cover has an outer surface comprising an indicia formed from the radioluminescent material.

13. A golf ball comprising a core and a cover, wherein the cover is coated with a radioluminescent material.

14. The golf ball of claim 13, wherein the radioluminescent material is present in an amount sufficient to emanate light without activation by UV or visible light.

15. The golf ball of claim 13, wherein the cover coating comprises paint, ink, paste, clearcoat, primer, or a mixture thereof.

16. The golf ball of claim 13, wherein the cover coating is further coated with a clearcoat.

17. The golf ball of claim 13, wherein the core comprises a center and an outer core layer.

18. The golf ball of claim 13, wherein the cover comprises an inner cover layer and an outer cover layer.

19. The golf ball of claim 13, wherein the golf ball has a coefficient of restitution of greater than about 0.78.

20. A golf ball comprising a core and a cover, wherein:

the core has a diameter of between about 1.5 and 1.59;

the cover comprises a radioluminescent powder and a thermoplastic material; and

the golf ball has a coefficient of restitution of greater than about 0.78;

and wherein the radioluminescent powder is present in an amount sufficient to emanate light without activation with UV or visible light.

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