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(54) **MULTI-LAYERED GOLF BALLS MADE WITH A THIOL-ENE COMPOSITION**

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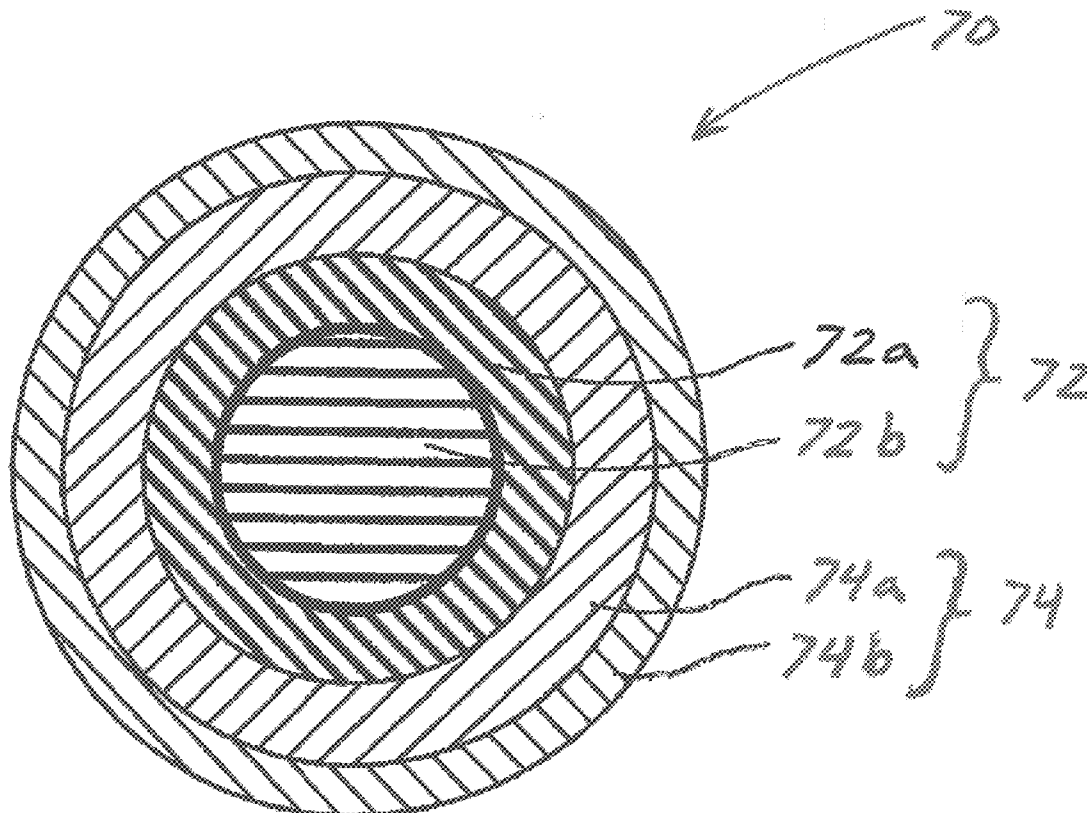
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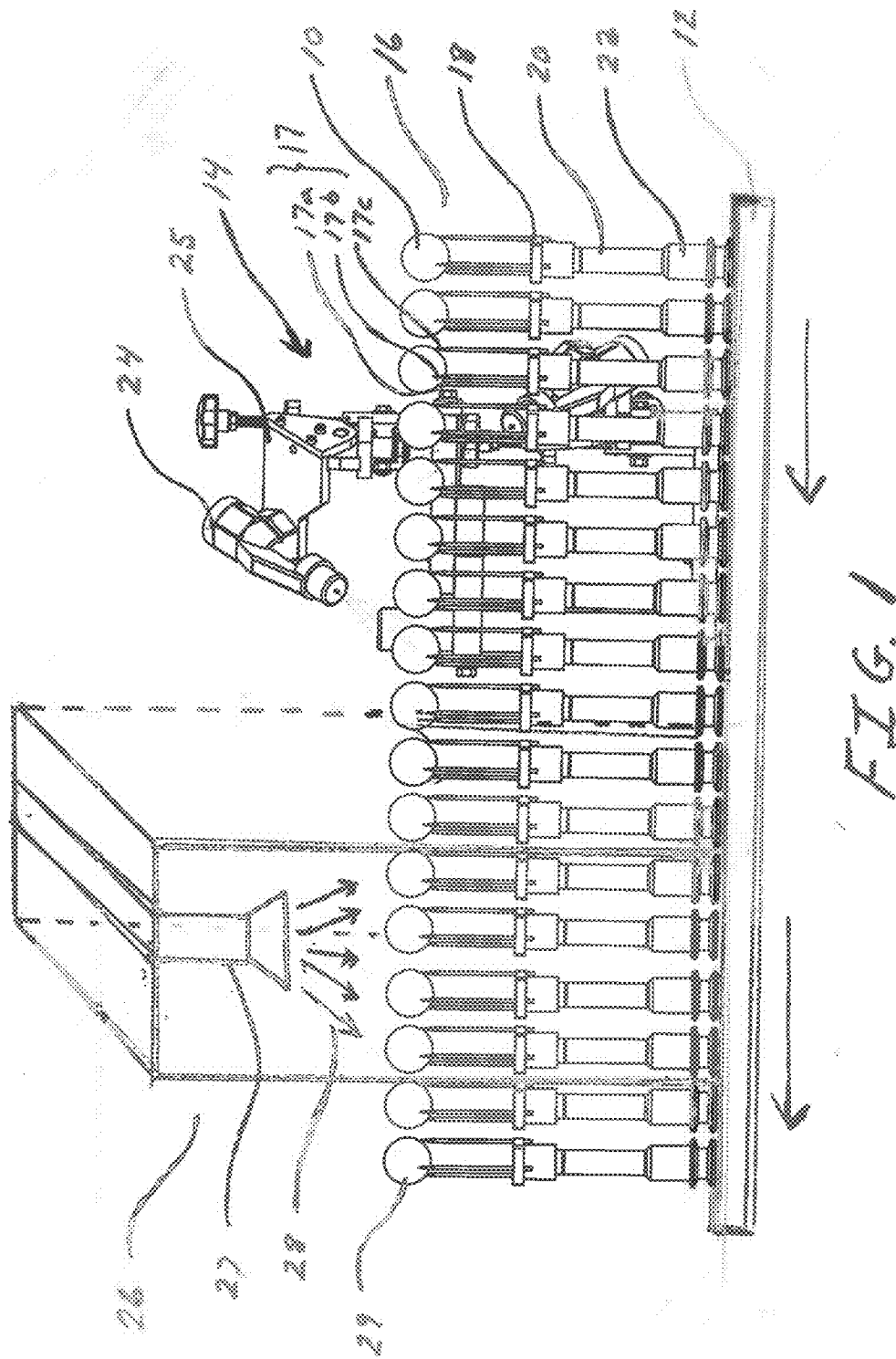
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(57) **ABSTRACT**
Methods for making multi-layered golf balls having at least one layer or coating made from a thiol-ene composition and the resultant golf balls are provided. A polymerizable composition comprising multifunctional thiol and -ene compounds is used to form the layer or coating. In one embodiment, the outer cover layer is made from the thiol-ene material. In another embodiment, a thiol-ene composition is applied as a protective coating over the outer cover layer. The thiol-ene layer or coating helps provide the ball with good impact durability and, toughness.

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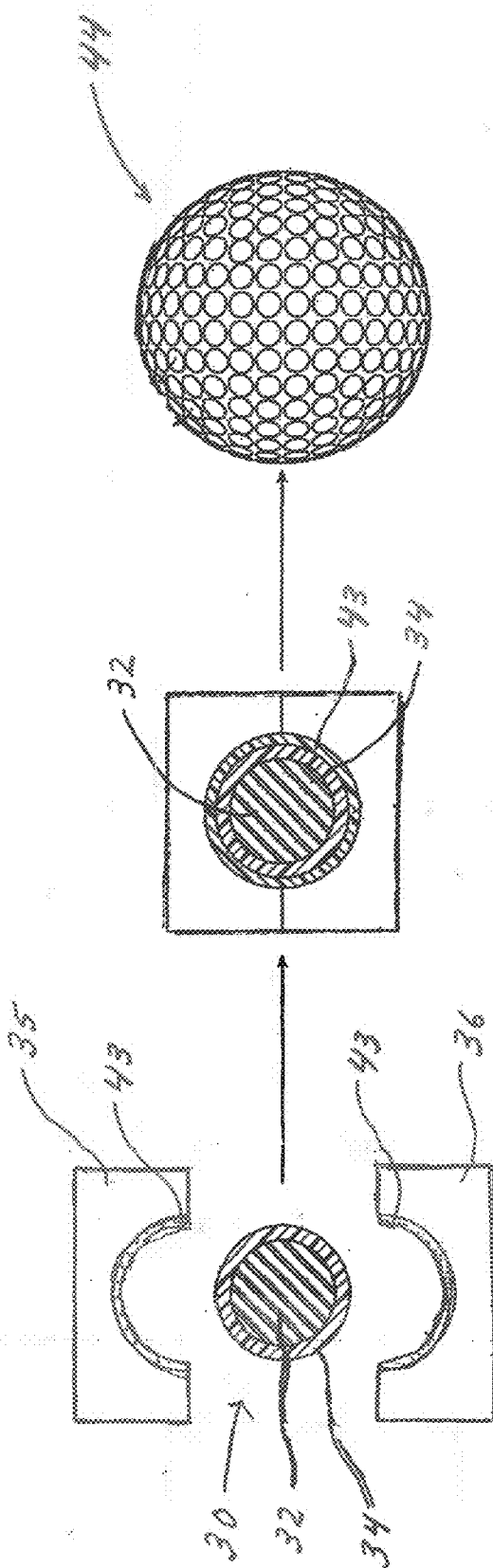


FIG. 2

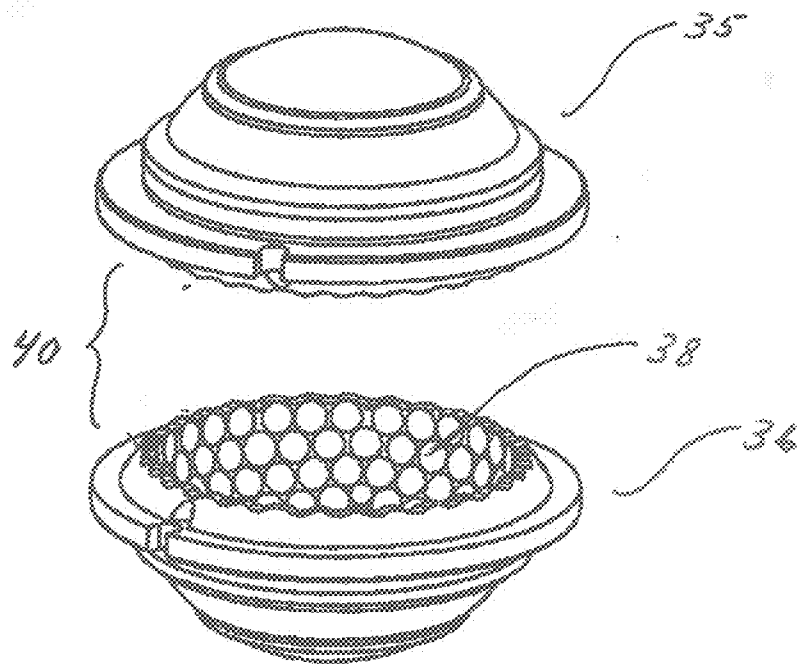


FIG. 3

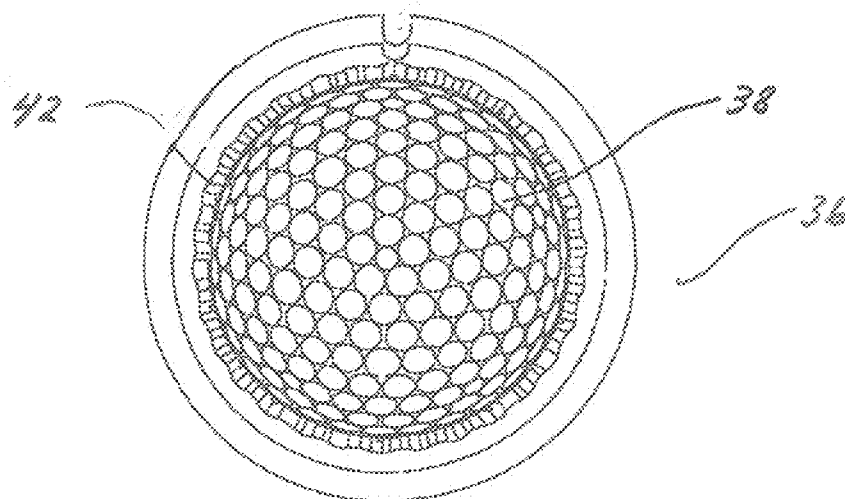


FIG. 3A

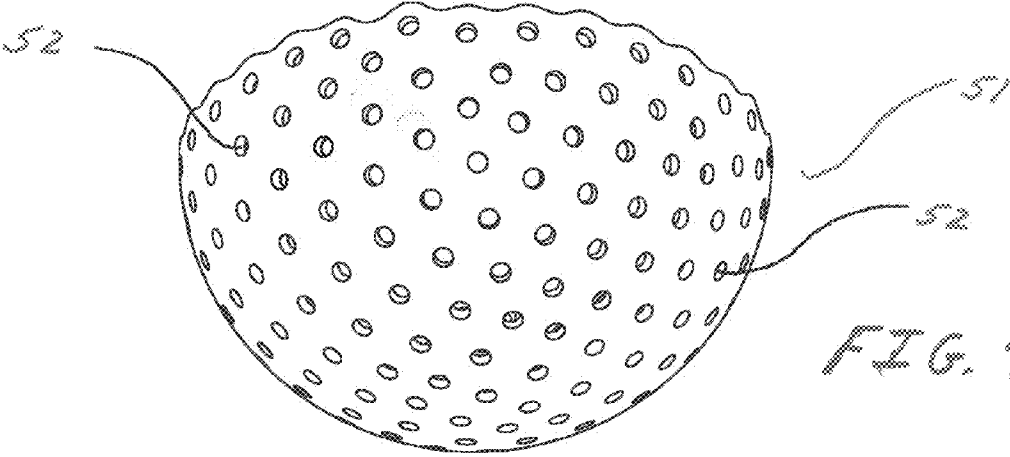
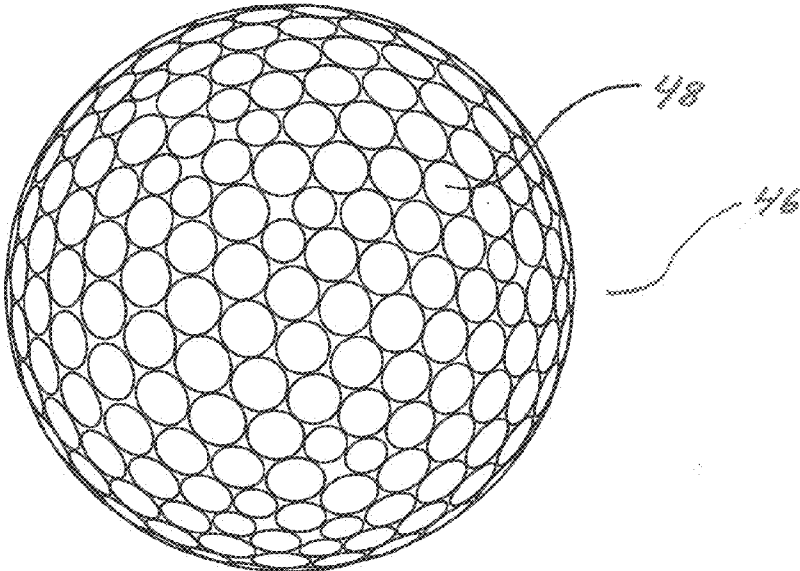
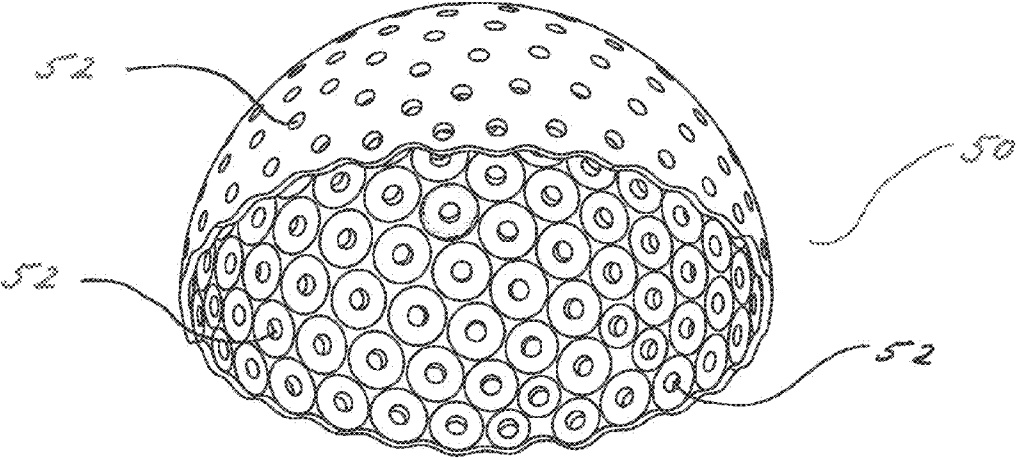


FIG. 4

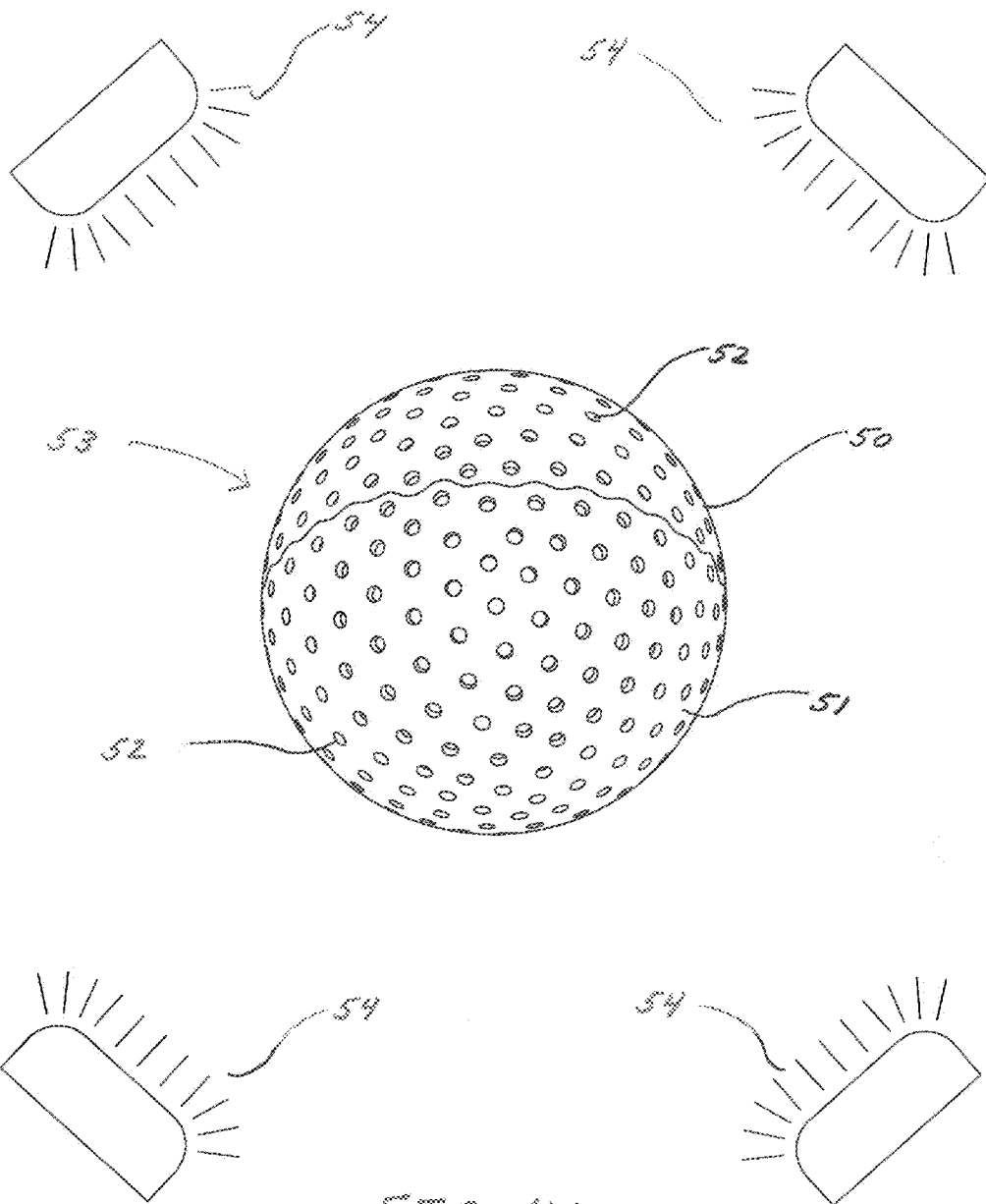


FIG. 4A

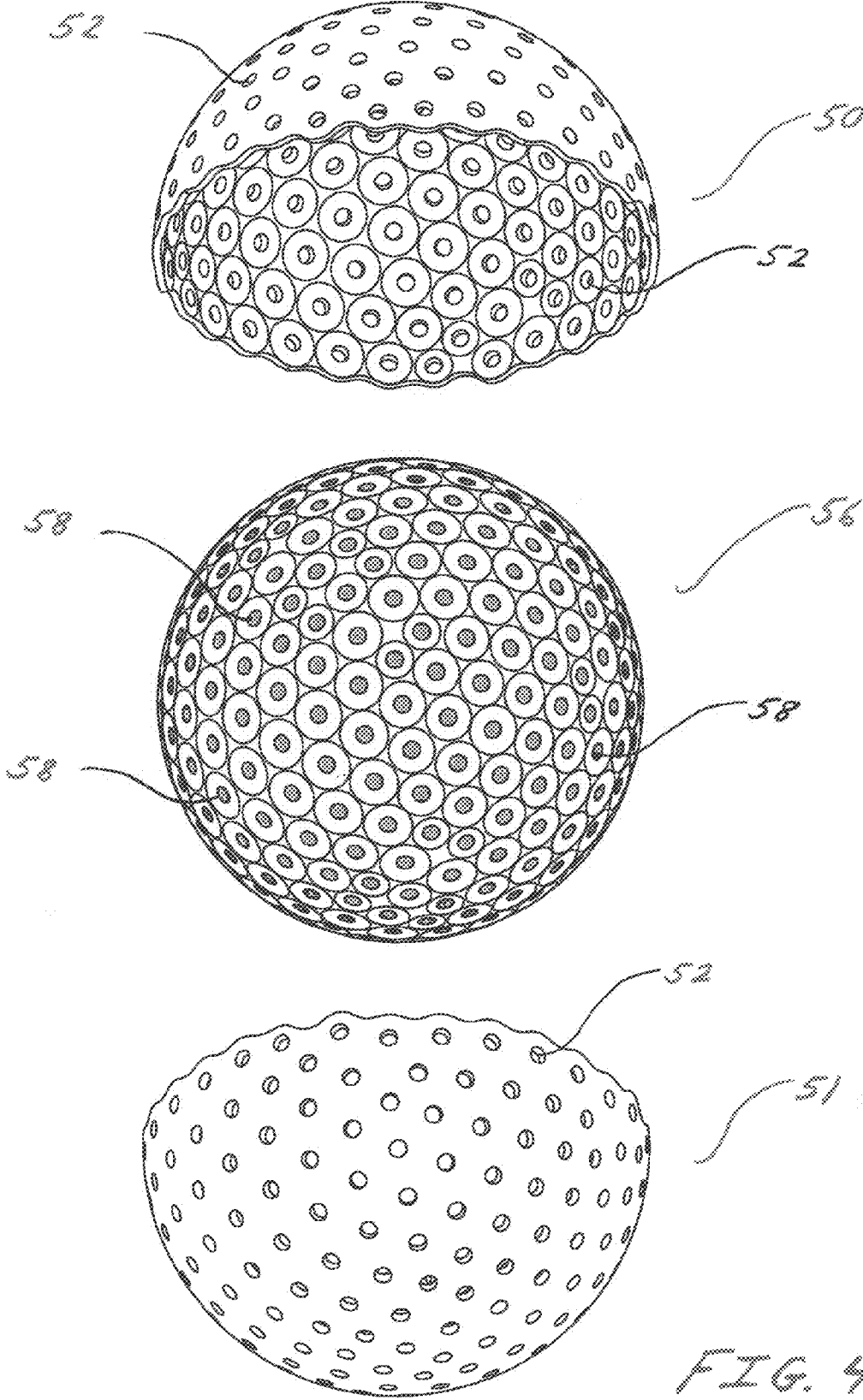


FIG. 4B

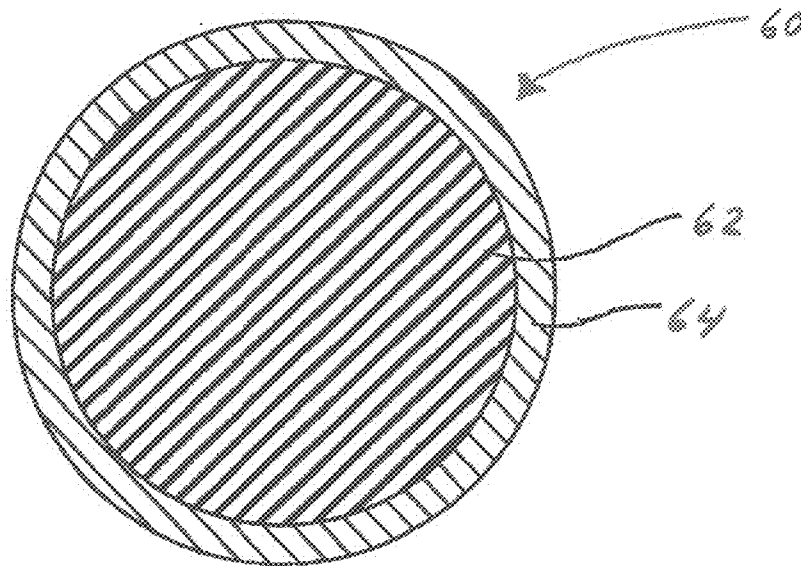


FIG. 5

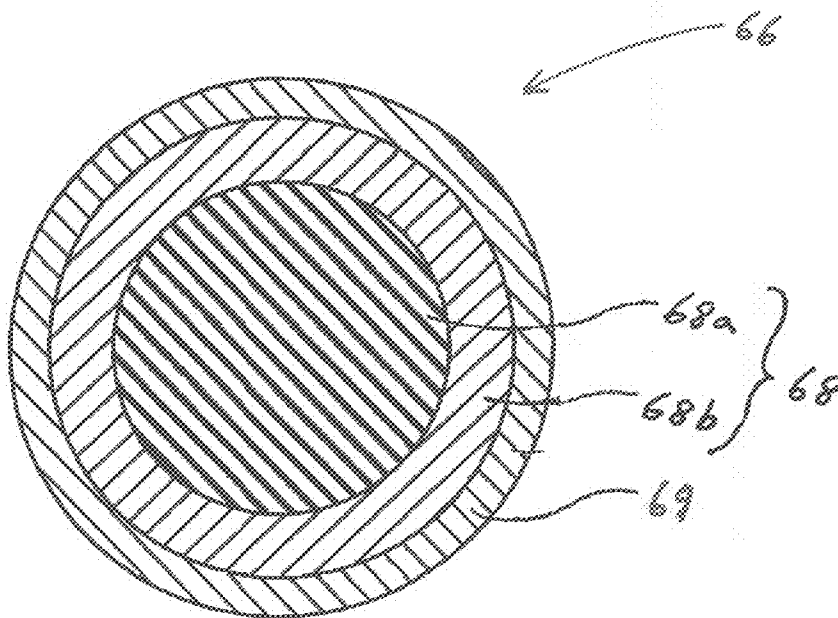


FIG. 6

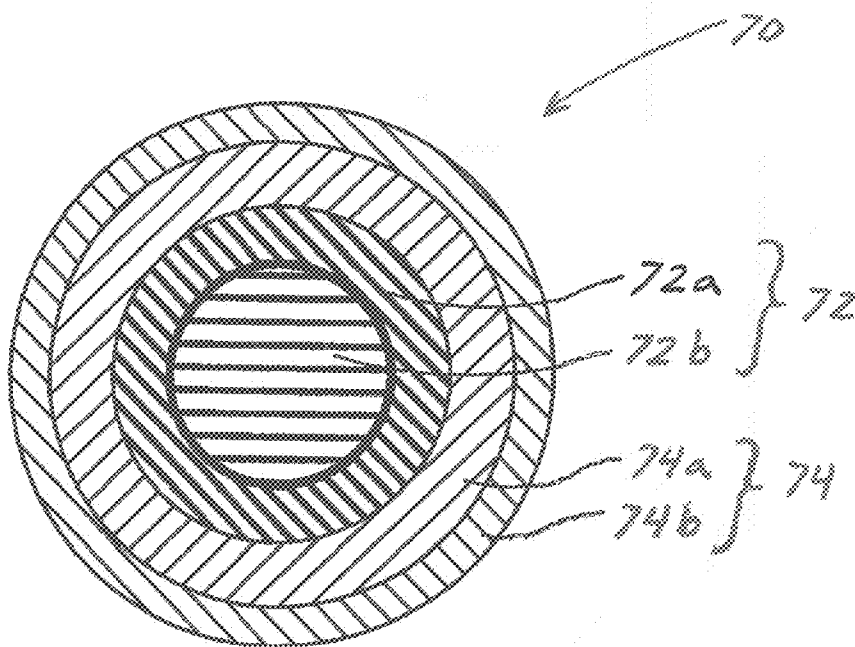


FIG. 7

MULTI-LAYERED GOLF BALLS MADE WITH A THIOL-ENE COMPOSITION

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates generally to methods for making multi-layered golf balls having at least one layer or coating made from a thiol-ene composition. A polymerizable composition comprising multifunctional thiol and -ene compounds is used to form the layer or coating. In one embodiment, the outer cover layer is made from the thiol-ene material. In another embodiment, a thiol-ene composition is applied as a protective coating over the outer cover layer. The golf ball further includes a core having at least one layer.

[0003] 2. Brief Review of the Related Art

[0004] Both professional and amateur golfer use multi-piece, solid golf balls today. Basically, a two-piece solid golf ball includes a solid inner core protected by an outer cover. The inner core is made of a natural or synthetic rubber such as polybutadiene, styrene butadiene, or polyisoprene. The cover surrounds the inner core and may be made of a variety of materials including ethylene acid copolymer ionomers, polyamides, polyesters, polyurethanes, and polyureas.

[0005] In recent years, three-piece, four-piece, and even five-piece balls have become more popular. New manufacturing technologies, lower material costs, and desirable ball playing-performance properties are contributing factors to the popularity of these multi-piece balls. Many golf balls used today have multi-layered cores comprising an inner core and at least one surrounding outer core layer. For example, the inner core may be made of a relatively soft and resilient material, while the outer core may be made of a harder and more rigid material. The "dual-core" sub-assembly is encapsulated by a cover of at least one layer to provide a final ball assembly. Different materials can be used to manufacture the core and cover and impart desirable properties to the final ball.

[0006] The core sub-assembly located inside of the golf ball acts as an engine or spring for the ball. Thus, the composition and construction of the core is a key factor in determining the resiliency and rebounding performance of the ball. In general, the rebounding performance of the ball is determined by calculating its initial velocity after being struck by the face of the golf club and its outgoing velocity after making impact with a hard surface. More particularly, the "Coefficient of Restitution" or "COR" of a golf ball refers to the ratio of a ball's rebound velocity to its initial incoming velocity when an air cannon fires the ball into a rigid vertical plate. The COR for a golf ball is written as a decimal value between zero and one. A golf ball may have different COR values at different initial velocities. The United States Golf Association (USGA) sets limits on the initial velocity of the ball so one objective of golf ball manufacturers is to maximize COR under such conditions. Balls with a higher rebound velocity have a higher COR value. Such golf balls rebound faster, retain more total energy when struck with a club, and have longer flight distance as opposed to balls with low COR values. These properties are particularly important for long distance shots. For example, balls having high resiliency and COR values tend to travel a far distance when struck by a driver club from a tee.

[0007] The durability, spin rate, and feel of the ball also are important properties. In general, the durability of the ball refers to the impact-resistance of the ball. Balls having low durability appear worn and damaged even when such balls are

used only for brief time periods. In some instances, the cover may be cracked or torn. The spin rate refers to the ball's rate of rotation after it is hit by a club. Balls having a relatively high spin rate are advantageous for short distance shots made with irons and wedges. Professional and highly skilled amateur golfers can place a back spin more easily on such balls. This helps a player better control the ball and improves shot accuracy and placement. By placing the right amount of spin on the ball, the player can get the ball to stop precisely on the green or place a fade on the ball during approach shots. On the other hand, recreational players who cannot intentionally control the spin of the ball when hitting it with a club are less likely to use high spin balls. For such players, the ball can spin sideways more easily and drift far-off the course, especially if it is hooked or sliced. Meanwhile, the "feel" of the ball generally refers to the sensation that a player experiences when striking the ball with the club and it is a difficult property to quantify. Most players prefer balls having a soft feel, because the player experience a more natural and comfortable sensation when their club face makes contact with these balls. Balls having a softer feel are particularly desirable when making short shots around the green, because the player senses more and can place a better touch on such balls. The feel of the ball primarily depends upon the hardness and compression of the ball.

[0008] Manufacturers of golf balls are constantly looking to different materials and ball constructions for improving the performance and other properties of the ball. For example, golf ball manufacturers have looked at making golf balls having relatively thin outer covers. Conventional thin covers provide the ball with a softer feel, and the player can place a spin on the ball and better control its flight pattern. The softer cover feels more natural. Players sense more control with these softer, relatively thin-covered golf balls.

[0009] For example, in Lutz et al., U.S. Pat. Nos. 6,783,808 and 6,706,332 a method of coating a thin-layered cover over a golf ball core is provided. The method involves providing a polymer material; creating a polymer particulate from the polymer material; fluidizing the polymer particulate; and coating the core or other ball component with a thin layer of the polymer material by placing the core within the fluidized particulate. Suitable polymers are described as including vinyl resins; polyolefins; polyurethanes; polyureas; polyamides; acrylic resins; and other thermoplastics and thermosets.

[0010] In Binette et al., US Patent Application Publication US 2011/0089607, multi-layered golf balls having an inner core, at least one intermediate layer, and outer cover are provided. The outer cover is made from an ultra-low melt index (ULMI) thermoplastic material using an in-molding coating process that involves applying a thin layer of the material to the interior surface of the cover mold members. Preferably, the ultra-low melt index material is a highly neutralized ionomer ethylene-based copolymer.

[0011] There are drawbacks, however, with such thin-covered golf balls, because the balls tend to have less durability, toughness, and cut/tear-resistance. The ball may appear excessively worn with scuff marks, cuts, and tears after continuous play on the golf course. It would be desirable to make relatively thin covers that could provide the ball with a combination of optimum properties. For example, the cover should have high impact durability, toughness, and cut/tear-resistance. At the same time, the cover should provide the ball with a soft feel so that a player feels comfortable and natural

when striking the ball with a club. The present invention provides new methods for making outer covers for golf balls as well as other component layers. The resulting ball has desirable playing-performance properties as well as other advantageous features and benefits.

SUMMARY OF THE INVENTION

[0012] The present invention provides golf balls having at least one layer or coating made from a composition comprising the reaction products of a multifunctional thiol compound and multifunctional ene compound. Preferably, the composition further comprises a polymerization initiator such as thermal initiators, photoinitiators, and mixtures thereof. The composition also may contain polymerization accelerators such as tertiary amines and polymerization inhibitors. In one version, the method used to make the golf ball generally involves the steps of: i) providing a golf ball comprising a spherical inner core and outer cover layer; and ii) coating a polymerizable composition comprising multifunctional thiol and ene compounds over the outer cover. The compounds react so that a golf ball comprising a polymerized thiol-ene outer coating is formed. In general, the coating has a thickness in the range of about 0.1 microns to about 100 microns. In one instance, the coating has a thickness in the range of about 10 microns to about 50 microns.

[0013] In another version, the method involves the steps of: i) providing a spherical inner core; and ii) molding a polymerizable composition comprising multifunctional thiol and ene compounds over the core. The compounds react so that a golf ball comprising a core and polymerized cover is formed. In general, the outer cover layer has a thickness in the range of about 0.010 to about 0.120 inches. For example, relatively thick covers having a thickness of about 0.070 to about 0.100 inches, or relatively thin covers having a thickness of about 0.010 to about 0.060 inches may be made.

[0014] In one preferred method, a photo-polymerizable composition comprising a multifunctional thiol compound and multifunctional ene compound, and a photoinitiator is molded over the core to form a cover. Then, visible or ultraviolet (UV) light is directed onto the cover composition so the composition is photo-polymerized. The coating method may use photo-masking techniques. For example, the method may involve molding a photo-polymerizable composition comprising multifunctional thiol and ene compounds, and a photoinitiator over the core to form a cover; placing a photo-mask over the cover that allows visible or ultra-violet (UV) light to contact selected areas of the cover composition; and directing visible or ultra-violet (UV) light onto the selected areas of the cover composition so these areas are photo-polymerized. The resulting golf ball comprises a core and cured cover. The outer cover layer made per the method of this invention has many advantageous properties including good impact durability, toughness, and cut/tear-resistance.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] The novel features that are characteristic of the present invention are set forth in the appended claims. However, the preferred embodiments of the invention, together with further objects and attendant advantages, are best understood by reference to the following detailed description in connection with the accompanying drawings in which:

[0016] FIG. 1 is a schematic diagram showing one embodiment for making a golf ball having a thiol-ene surface coating in accordance with the present invention;

[0017] FIG. 2 is a schematic diagram showing one embodiment for making a golf ball having a thiol-ene outer cover layer in accordance with the present invention;

[0018] FIG. 3 is a perspective view of upper and lower mold cavities that may be used in accordance with the present invention;

[0019] FIG. 3A is a top-down view of the lower mold cavity shown in FIG. 3;

[0020] FIG. 4 is a perspective view of upper and lower mask members and a golf ball having a thiol-ene outer cover in accordance with the present invention;

[0021] FIG. 4A is a perspective view of the upper and lower mask members in FIG. 4 mated together and encapsulating the ball with ultraviolet (UV) lamps emitting light radiation onto the assembly;

[0022] FIG. 4B is a perspective view of the mated upper and lower mask members in FIG. 4A being removed from the underlying ball, wherein the ball has cover layer with selected cured areas;

[0023] FIG. 5 is a cross-sectional view of a two-piece golf ball having an inner core and a cover layer made in accordance with the present invention;

[0024] FIG. 6 is a cross-sectional view of a three-piece golf ball having a dual-core comprising an inner core and outer core and a cover layer made in accordance with the present invention; and

[0025] FIG. 7 is a cross-sectional view of a four-piece golf ball having a dual-core comprising an inner core and outer core, an inner cover layer, and an outer cover layer made in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0026] Golf Ball Constructions

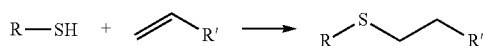
[0027] Golf balls having various constructions may be made in accordance with this invention. For example, golf balls having two-piece, three-piece, four-piece, and five-piece constructions may be made. Representative illustrations of such golf ball constructions are provided and discussed further below. The term, "layer" as used herein means generally any spherical portion of the golf ball. More particularly, in one version, a two-piece golf ball containing an inner core and outer cover may be made. A three-piece golf ball containing an inner core and outer cover, wherein a casing layer is disposed between the core and cover, also may be made. In another version, a four-piece golf ball containing a dual-core (inner core [center] and outer core layers); an inner cover layer; and outer cover layer may be made. In yet another example, a five-piece golf ball containing a dual-core; a casing layer; and dual-cover (inner cover and outer cover layers) is made. As used herein, the term, "casing layer" means a layer of the ball disposed between inner core and outer cover. The casing layer also may be referred to as a mantle or intermediate layer or inner cover layer. The diameter and thickness of the different layers along with properties such as hardness and compression may vary depending upon the construction and desired playing performance properties of the golf ball.

[0028] Polymerizable Compositions

[0029] The present invention relates to golf balls having at least one layer or coating made from a composition comprising the reaction products of a multifunctional thiol compound

and multifunctional-ene compound. In the method, a polymerizable composition comprising the multifunctional thiol and ene compounds is prepared. The compounds react to form a thiol-ene compound. The resulting composition may be used to form any component of the golf ball, for example, an outer cover layer. The thiol-ene composition of this invention is primarily discussed herein as being suitable for producing an outer cover layer for a golf ball. However, it is recognized the thiol-ene composition may be used for producing inner and outer core layers, casing layers, inner covers, outer surface coatings and any other suitable component for the golf ball in accordance with this invention.

[0030] As discussed above, thiol-ene reactions involve a reaction between a thiol and unsaturated compounds. In the reaction, there is an addition of a S—H bond across a double or triple bond normally by a free-radical mechanism. The reaction is often referred to as “click chemistry”, because it is so quick and efficient and high-yielding. The thiol-ene reaction is generally shown below:



[0031] Thiol Compounds

[0032] Multifunctional thiol compounds are generally known in the art and these compounds can be used in accordance with this invention. For example, such thiol compounds are described in Ellison et al., U.S. Patent Application Publication US 2006/0128826, the disclosure of which is hereby incorporated by reference. In general, the multifunctional thiol compounds contain two or more thiol (“mercapto”; —SH) groups per molecule. The multifunctional thiol compounds can be monomers or oligomers having two or more functional thiol groups and be of any molecular weight. Suitable thiol monomers include, for example, alkyl thiol compounds such as 1,2-dimercaptoethane, 1,6-dimercaptohexane, neopentantetrathiol, and the like, pentaerythritol tetra (3-mercapto propionate), 2,2-bis(mercaptomethyl)-1,3-propanedithiol, and the like, aryl thiol compounds such as 4-ethylbenzene-1,3-dithiol, 1,3-diphenylpropane-2,2-dithiol, 4,5-dimethylbenzene-1,3-dithiol, 1,3,5-benzenetriethiol, glycol dimercaptoacetate, glycol dimercaptopropionate, pentaerythritol tetrathio glycolate, trimethylolpropane trithio glycolate, and the like.

[0033] Other examples of thiol monomers include: pentaerythritol tetramercaptopropionate (PETMP); 1-Octanethiol; Butyl 3-mercaptopropionate; 2,4,6-trioxo-1,3,5-triazina-triy (triethyl-tris(3-mercapto propionate)); 1,6-Hexanedithiol; 2,5-dimercaptomethyl-1,4-dithiane, pentaerythritol tetramercaptoacetate, trimethylolpropane trimercaptoacetate, 2,3-dimercapto-1-propanol, 2-mercaptoethylsulfide, 2,3-(dimercaptoethylthio)-1-mercaptopropane, 1,2,3-trimercaptopropane, toluenedithiol, xylylenedithiol, 1,8-octanedithiol, 1-hexanethiol (Sigma-Aldrich, Milwaukee, Wis.); and trimethylolpropane tris(3-mercaptopropionate), and glycol dimercaptopropionate (Evans Chemetics LP, Iselin, N.J.). Suitable oligomeric multifunctional thiols include, for example, polysiloxanes, polymers having a siloxane-based backbone and further comprising two or more thioalkyl groups pendent from the backbone.

[0034] Ene Compounds

[0035] Multifunctional-ene compounds also are generally known in the art and are described, for example, in the above-

mentioned '826 Publication. In general, monomers having “-ene” or vinyl functional groups suitable for the present invention include any monomer having one, or preferably more functional vinyl groups, i.e., reacting “C=C” or “C≡C” groups. The “-ene” monomer can be selected from one or more compounds having vinyl functional groups. Vinyl functional groups can be selected from, for example, vinyl ether, vinyl ester, allyl ether, norbornene, diene, propenyl, alkene, alkyne, N-vinyl amide, unsaturated ester, N-substituted maleimides, and styrene moieties.

[0036] Multifunctional ethylenically unsaturated compounds are suitable “-ene compounds” that can be used in accordance with this invention. The ethylenically unsaturated groups include a carbon-carbon double bond such as those found in the following functional groups: allyl, vinyl, acryloxy, methacryloxy, acrylamido, methacrylamido, acetylenyl, maleimido, and the like.

[0037] Suitable multifunctional ethylenically unsaturated compounds include, for example, compounds containing a core structure linked to ethylenically unsaturated groups, optionally via a linking group. The linking group can be an ether, ester, amide, urethane, carbamate, or carbonate functional group. In some instances, the linking group is part of the ethylenically unsaturated group, for instance an acryloxy or acrylamido group. The core group can be an alkyl (straight and branched chain alkyl groups), aryl (e.g. phenyl), polyether, siloxane, urethane, or other core structure and oligomers thereof. Examples of multifunctional ethylenically unsaturated compounds include tri-allyl isocyanurate; tri-vinyl isocyanurate; diallyl maleate; diallylether bisphenol A; ortho diallyl bisphenol A; triallyl trimellitate; tri(meth)acryl triols such as trimethylolpropane tri(meth)acrylate; triallyl triols such as 1-(allyloxy)-2,2-bis((allyloxy)methyl)butane; polyvinyl polyols such as 1-(vinylloxy)-2,2-bis((vinylloxy)methyl)butane; polyallyl polyols; polyvinyl polyetherpolyols; polyallyl polyetherpolyol; and the like.

[0038] Other suitable-ene compounds include Triallyl-1,3,5-triazine-2,4,6-trione (TATATO); Triethyleneglycol divinyl ether (TEGDVE); Trimethylolpropane diallyl ether; Dodecyl vinyl ether (DDVE); 1,6-heptadiyne; 1,7-octadiyne; bis-2,2-[4-(2-[norborn-2-ene-5-carboxylate]ethoxy)phenyl]propane (BPAEDN); 1,6-hexanediol di-(endo,exo-norborn-2-ene-5-carboxylate) (HDDN); trimethylolpropane tri-(norborn-2-ene-5-carboxylate) (TMPTN); pentaerythritoltri-(norborn-2-ene-5-carboxylate) (PTN3); pentaerythritol tetra-(norborn-2-ene-5-carboxylate) (PTN4); tricyclodecane dimethanol di-(endo,exo-norborn-2-ene-5-carboxylate) (TCDMDN); and di(trimethylolpropane)tetra-(norborn-2-ene-5-carboxylate) (DTMPTN); and mixtures thereof.

[0039] Initiators

[0040] It is recognized the thiol compound and -ene compound reaction can take place in the absence of polymerization initiators. However, in the majority of cases, a polymerization initiator is included in the composition. The initiator helps drive the reaction so there is a faster cure rate. Suitable polymerization initiators include, for example, thermal initiators such as peroxide and azo compounds; and photoinitiators such as visible and ultra-violet (UV) light activated initiators. In other instances, high-energy radiation such as electrons, neutrons, protons, gamma rays, x-rays, helium nuclei, and the like can be used to irradiate the composition. Normally, when using such high-energy radiation, the dosage is greater than 1 megarad, particularly in the range of about 2 to 15 megarads.

[0041] In one embodiment, the composition contains a thermal initiator such as peroxide. Suitable organic peroxides include, but are not limited to, dicumyl peroxide; n-butyl-4,4-di(t-butylperoxy) valerate; 1,1-di(t-butylperoxy)3,3,5-trimethylcyclohexane; 2,5-dimethyl-2,5-di(t-butylperoxy) hexane; di-t-butyl peroxide; di-t-amyl peroxide; t-butyl peroxide; t-butyl cumyl peroxide; 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3; di(2-t-butyl-peroxyisopropyl)benzene; dilauroyl peroxide; dibenzoyl peroxide; t-butyl hydroperoxide; and combinations thereof. In a particular embodiment, the free radical initiator is dicumyl peroxide, including, but not limited to Perkadox® BC, commercially available from Akzo Nobel. Suitable azo compounds include, but are not limited to, azobisisobutyronitrile (AIBN).

[0042] In another embodiment, the composition contains a photoinitiator and the process is referred to as photo-polymerization. Conventional photoinitiators may be used. Suitable photoinitiators include phosphine oxide photoinitiators; ketone-based photoinitiators, such as hydroxy- and alkoxy-alkyl phenyl ketones, and thioalkylphenyl morpholinoalkyl ketones; benzoin ether photoinitiators; and the like. In general, photoinitiators that are responsive to ultraviolet (UV) light (wavelength of about 200 to about 400 nm) and/or photoinitiators that are responsive to visible light (wavelength of about 380 to about 780 nm) may be used.

[0043] Visible light photoinitiators which are suitable for the present invention include the initiators described in Sullivan et al., U.S. Pat. No. 7,198,576, the disclosure of which is hereby incorporated by reference. These photoinitiators include fluorene derivatives such as 5,7-diiodo-3-butoxy-6-fluorene (with a maximum absorbance at 470 nm); 2,4,5,7-tetraiodo-3-hydroxy-6-fluorene (with a maximum absorbance at 535 nm); and 2,4,5,7-tetraiodo-9-cyano-3-hydroxy-6-fluorene (with a maximum absorbance at 635 nm), all of which are available from Spectra Group Limited, Inc. Other useful visible light photoinitiators include, but are not limited to, titanocene photoinitiators, e.g., fluorinated diaryl titanocenes; ketocoumarine photoinitiators, e.g., 3-ketocoumarine; acridine dyes, e.g., acriflavine; xanthene dyes, e.g., rose bengal or fluorescein; azine dyes, thiazine dyes, e.g., methylene blue; polymethine dyes, e.g., cyanines or merocyanines; diaryliodonium salts; triarylsulfonium salts; chromophore substituted halomethyl-s-triazines; halomethyl oxadiazoles; and combinations thereof.

[0044] Suitable ultra-violet (UV) light photoinitiators include, for example, benzophenone and derivatives thereof, acetophenone, benzoin, benzoin methyl ether, benzoin butyl ether, acyloin, alcyloin ether, Michler's ketone, xanthone, thioxanthone, propiophenone, fluorenone, carbazole, diethoxyacetophenone, 2-, 3-, and 4-methylacetophenone, 2-, 3-, and 4-methoxy-acetophenone, 2- and 3-chloroxanthones, 2- and 3-chlorothioxanthones, 2-acetyl-4-methylphenylacetate, 2,2'-dimethoxy-2-phenylacetophenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, 3- and 4-allylacetophenone, p-diacetylbenzene, 3-chloro-2-nonyl-xanthone, 2-chlorobenzophenone, 4-methoxybenzophenone, 2-chloro-4'-methylbenzophenone, 4-chloro-4'-methylbenzophenone, 3-methylbenzophenone, 4-tertbutylbenzophenone, isobutyl ether-benzoic acetate, bezilic acid, amino benzoate, methyl blue, 2,2-diethoxyacetophenone, 9,10-phenanthrenequinone, 2-methyl anthraquinone, 2-ethyl anthraquinone, 1-tert-butyl anthraquinone, 1,4-naphthaquinone, 2-isopropylthioxanthone, 2-methylthioxanthone, 2-decylthioxanthone, 2-dodecylthioxanthone, oligo

(2-hydroxy-2-methyl-1-(4-(1-methylvinyl)phenyl)propanone), 2,4,6-trimethylbenzophenone, 4-methylbenzophenone, 2,2-dimethoxy-1,2-diphenylethane, 2-butoxy-1,2-diphenylethane, 2-(2-methyl propoxy)-1,2-diphenylethane, alpha hydroxy ketones such as 2-alpha hydroxy ketone, and combinations of the foregoing.

[0045] Other examples of suitable photoinitiators include 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone; 2-hydroxy-2-methylpropiophenone; benzophenone; trimethylbenzophenone; methylbenzophenone; 1-hydroxycyclohexylphenyl ketone; isopropyl thioxanthone; 2,2-dimethyl-2-hydroxy-acetophenone; 2,2-dimethoxy-2-phenylacetophenone; 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one; 2,4,6-trimethylbenzyl-diphenylphosphine oxide; 1-chloro-4-propoxythioxanthone; benzophenone; bis(2,6-dimethoxybenzoyl)-2,4,4-trimethyl pentyl phosphine oxide; 1-phenyl-2-hydroxy-2-methyl propanone; bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide; camphorquinone; and combinations of the foregoing; and the like. In particular, other visible light photoinitiators include bis acyl phosphine oxides (BAPO) such as phenyl bis(2,4,6-trimethyl benzoyl)phosphine oxide (Irgacure 819, Ciba); and other ultraviolet (UV) light photoinitiators include an alpha-hydroxyketone, such as 1-hydroxy-cyclohexyl-phenylketone (Irgacure 184, Ciba); or a benzyl dimethyl-ketal, such as 2,2-dimethoxy-2-phenylacetophenone (DMPA, e.g. Irgacure 651, Ciba).

[0046] One or more polymerization initiators may be used in accordance with this invention. Also, any suitable combination of initiators may be used. The thickness and opacity of the cover or other component layer/coating are important factors in considering the type and amount of polymerization initiator that should be employed. For example, if the cover layer (or coating) is relatively thick, then a thermal initiator solely or a combination of thermal and photo initiators are preferably used. On the other hand, if the cover layer (or coating) is relatively thin, then a thermal initiator by itself; a photo initiator by itself; or a combination of thermal and photo initiators may be used. If the cover layer (or coating) has a relatively high degree of opacity (for example, it is highly pigmented), a thermal initiator preferably is used. Combinations of a thermal initiator with a nominal amount of photo initiator also may be used. Conversely, if the cover layer (or coating) is relatively transparent, then a thermal initiator by itself; or a photo initiator by itself may be used. Combinations of a thermal initiator with a photo initiator (for example, 50% thermal/50% photo) also may be used.

[0047] The polymerization initiators are normally used in amounts of about 0.1 to about 10, particularly about 0.25 to about 5, and more particularly about 0.5 to about 1 weight percent based on total weight of thiol-ene composition. In one case, the ratio of photoinitiator to thermal initiator is about 1:1. In other embodiments, the ratio of photoinitiator to thermal initiator is greater or less than 1:1. For example, the ratio of photoinitiator to thermal initiator may be in the range of 2:1 to 10:1. In other embodiments, the ratio of photoinitiator to thermal initiator is in the range of 1:2 to 1:10.

[0048] In addition, polymerization accelerators can be included in the composition. These include amine accelerators such as various organic tertiary amines. These accelerators include ethyl-para-(dimethylamino)benzoate (EDAB) 2-[4-(dimethylamino)phenyl]ethanol, N,N-dimethyl-p-toluidine (DMPT), bis(hydroxyethyl)-p-toluidine, triethanolamine, and the like. Such accelerators are generally present

in the composition at about 0.1 to about 5.0 weight percent. The composition also may include polymerization inhibitors that act as scavengers to trap free radicals and extend the composition's working and setting times. The polymerization inhibitors prevent the composition from curing too rapidly. Polymerization inhibitor such as, for example, butylated hydroxytoluene (BHT); hydroquinone; hydroquinone monomethyl ether; benzoquinone; chloranil; phenol; butyl hydroxyaniline (BHA); tertiary butyl hydroquinone (TBHQ); tocopherol (Vitamin E); and the like. Such accelerators are generally present in the composition at about 0.1 to about 3.0 weight percent.

[0049] As described further below, the inner core preferably is formed from a rubber composition using compression or injection molding or other standard techniques as known in the art. Then, the casing layer (optional) and cover layer are applied over the core structure. The core structure and any casing layers are commonly referred to as the ball "sub-assembly."

[0050] As shown in FIG. 1, in one version, the thiol-ene composition is applied as a protective coating over the outer cover. The composition comprises the thiol and -ene compounds and other ingredients as discussed above. As discussed above, in one embodiment, the reactive composition contains only a thermal initiator. In another embodiment, the reactive composition contains only a photoinitiator. Mixture of thermal and photoinitiators also may be used. In this coating method, the golf balls (10) are first cleaned and dried in a cleaning station (not shown). This cleaning/drying of the balls' surfaces helps improve adhesion of the coating that will be applied. The balls (10) are carried by a conveyor belt (12) or other suitable transporting means through a spray-coating station (14). Each golf ball (10) is held in a spindle cup (16) by prongs (17). Typically, each cup (16) has three prongs (17a, 17b, and 17c) projecting upwardly from a spindle platform (18) which is supported by a shaft (20) and shaft base (22). As each spindle cup (16) approaches the spray-coating station (14), the cups (16) rotate about a vertical axis extending through the center of each shaft (20). The ball (10) is rotated within the cup (16) so that the entire surface of the ball may be treated with the coating. The spray guns (24) mounted on platform (25) may be held in a fixed position or may be movable with respect to the balls (10). The balls are then transported via the conveyor belt (12) through a curing tunnel (26), wherein the balls are cured.

[0051] The curing tunnel (26) may include a thermal lamp that emits heat energy and/or a light source that emits light energy (for example, visible and/or ultraviolet (UV) light), and this lamp/light source is generally indicated at (27). Any conventional curing light may be used in accordance with this invention. These light sources include thermal lamps and visible and ultraviolet curing lights known in the industry. The specific light source used and the luminosity, wavelength, filters, and the like of the light will depend upon the composition of the polymerizable material, thickness of the coating (layer); and other factors. The thermal and/or light energy (28) is directed onto the outer cover of the ball. This drives the polymerization reaction so the coating cures and hardens. A thiol-ene composition is formed after the surface is cured, and the surface-coated balls (29) exit the curing tunnel (26).

[0052] In yet another version, an outer surface coating comprising the above-discussed polymerizable thiol-ene composition may be applied onto the ball using a dipping method.

Here, the golf balls may be immersed in a treatment bath containing the thiol-ene composition. For example, the ball may be held by a pair of tongs and then dipped into the bath. The coated ball is then removed from the bath and treated with visible or UV light to cure and harden the coating as discussed above.

[0053] The thickness of the coating is typically in the range of about 0.1 microns to about 100 microns, preferably from about 10 microns to about 50 microns, more preferably from about 15 microns to about 25. Preferably, the coating has a thickness of less than about 5 mils (0.005 inches) and more preferably less than 3 mils (0.003 inches). In one instance, the coating has a thickness in the range of about 0.5 to about 2.5 mils (0.0005 to 0.002 inches).

[0054] In another version, an outer cover layer comprising the above-discussed polymerizable composition containing the multifunctional thiol and -ene compounds may be applied over the ball sub-assembly. The outer cover layer may be formed using a suitable technique such as, for example, compression-molding, flip-molding, injection-molding, retractable pin injection-molding, reaction injection-molding (RIM), liquid injection-molding, casting, spraying, powder-coating, vacuum-coating, flow-coating, dipping, spin-coating, and the like.

[0055] For example, as illustrated in FIG. 2, in one embodiment, a casting method is used to form an outer cover comprising the thiol-ene composition. Here, the golf ball sub-assembly (30), comprising a solid core (32) surrounded by a casing layer (34), is placed in a mold cavity defined by the upper and lower mold cavities (35, 36).

[0056] Referring to FIGS. 3 and 3A, the mold cavities (35, 36) are shown in more detail. Each mold cavity has a curved inner surface defining an inverted dimple pattern (38). When the mold cavities are mated together, they will define an interior spherical cavity (40) that forms the cover for the ball. The mold cavities are mated together along a parting line (42) that creates an equator (or seam) for the finished ball. The cover composition encapsulates the inner ball sub-assembly and forms a unitary cover structure. In particular, the cover composition conforms to the interior geometry of the mold cavities to form a dimple pattern on the surface of the ball. The mold cavities may have any suitable dimple arrangement such as, for example, icosahedral, octahedral, cube-octahedral, di-pyramid, and the like. The dimples may be circular, oval, triangular, square, pentagonal, hexagonal, heptagonal, octagonal, and the like.

[0057] Referring back to FIG. 2, the upper and lower mold cavities (35, 36) can be preheated and filled with the reactive composition (43) comprising the thiol and ene compounds and other ingredients as discussed above. In one preferred embodiment, as shown in FIG. 2, the reactive composition (43) contains a thermal initiator. After the reactive mixture has resided in the lower mold cavity (36) for a sufficient time period, the ball sub-assembly (30) is lowered at a controlled speed into the reacting mixture. Then, the upper half-mold (35) can be mated with the lower half-mold (36). A polymerization reaction occurs when the multifunctional thiol and -ene compounds, and thermal initiator are mixed together. This reaction continues until the material solidifies around the ball sub-assembly (30). Then, the molded balls (44) are cooled in the mold and removed when the molded cover layer is hard enough to be handled without deforming.

[0058] In general, the outer cover layer is a thicker material than the above-discussed thiol-ene coating that is applied

over the outer cover. The cover layer has greater integrity, mechanical strength and durability than the sprayed or dipped-on coating. In one embodiment, the outer cover has a relatively large thickness and may be within a range of about 0.060 to about 0.120 inches, particularly about 0.070 to about 0.100 inches, and even more particularly about 0.080 to about 0.090 inches. In another embodiment, the outer cover has a relatively small thickness. For example, the thickness of the outer cover layer may be within a range of about 0.010 to about 0.070 inches, particularly about 0.020 to about 0.060 inches, and even more particularly about 0.030 to about 0.050 inches. In one embodiment, the thickness of the coating is greater than 0.040 inches and in the range of 0.045 to 0.085 inches.

[0059] The cover layer formed by the composition of this invention has many advantageous properties including good impact durability, toughness, and cut/tear-resistance. In one embodiment, the cover layer formed by the method of this invention is relatively thin and has uniform thickness. At the same time, the cover is durable and tough. In addition, the cover layer of this invention helps impart high resiliency to the golf balls. Preferably, the golf ball has a COR of at least 0.700 more preferably about 0.720 or greater; and even more preferably about 0.750 to 0.850 or greater. This allows players to generate greater ball velocity off the tee and achieve greater distance. At the same time, the relatively thin cover layers means that a player will have a more comfortable and natural feeling when striking the ball with a club. The ball is more playable and its flight path can be controlled more easily. This control allows the player to make better approach shots near the green. The compression of the ball is generally in the range of about 40 to about 110 and more preferably in the range of about 70 to about 100.

[0060] In another embodiment of the method of this invention, photo-masking is used on the surface of the outer cover (or coating) to create a patterned surface thereon. In this method, a core structure is coated with a first layer of the photo-polymerizable composition comprising the multifunctional thiol and ene compounds. Spraying, dipping, and other coating techniques as discussed above may be used to coat this layer of photo-polymerizable composition. This first coating may be referred to as a primer coating. The primer coating is then light-cured so that it substantially hardens. The primer coating may be partially or fully-cured at this point. Then, a second layer of the photo-polymerizable composition comprising the multifunctional thiol and ene compounds is coated over the primer layer using spraying, dipping, or other coating methods. This second coating may be referred to as a top-coating.

[0061] A mask having light-limiting blocks (solid segments) that prevent light from reaching certain areas of the photo-polymerizable material is placed over the top-coating. The solid segments in the mask substantially block the transmission of light. Thus, some of the light energy is prevented from reaching the coating, and these areas do not substantially cure. The top-coating is then treated with visible and/or ultraviolet curing light or other radiation. During this curing step, there may be some blending and fusing of the photo-polymerizable material of the primer layer and photo-polymerizable material of the top-coating. The resulting golf ball having the cured cover layer may then be cooled. In a final step, the golf ball is treated with a solution to wash away any uncured material in the cover layer.

[0062] When the photo-polymerizable composition is exposed to the curing light, those areas of the composition lying underneath the light-blocking segments will not be exposed to the same amount of light that the unmasked material is exposed to. As a result, there will be different polymerization rates, and the physical properties of the masked and non-masked portions will be different. Various mask patterns may be used and they will have different effects on polymerization rate and the related properties of the material. The mask can be made from plastic films or molds or any other suitable material that will not allow substantial light transmission through the masked segments.

[0063] Referring to FIGS. 4, 4A, and 4B, one version of a photo-masking coating method of this invention is shown. Here, the ball (46) includes an outer cover layer (or coating) of the photo-polymerizable composition comprising the multifunctional thiol and ene compounds (48). The photo-mask includes upper and lower hemisphere-shaped shells (50, 51). The upper and lower shells (50, 51) have relatively small apertures (52) that allow curing light to be transmitted onto the photo-polymerizable material (48). As discussed above, the mask can have any desirable pattern of apertures to generate different curing patterns. Masks having openings (52) with different geometric shapes and dimensions can be used resulting in different curing effects. For example, positively and negatively-configured masks may be used to form different extending segments in the layer that are cured. In turn, mechanical properties such as hardness, durability, surface roughness, and the like will vary based on the mask patterns used over the photo-polymerizable material. In Step 2 (FIG. 4A), the upper and lower shells (50, 51) are mated together so that they encapsulate the ball (46). Then, the entire assembly (upper/lower shells and underlying ball) generally indicate at (53) is treated with visible and/or ultraviolet curing light or other radiation (54). The radiation (54) is transmitted through the openings (52) in the mask to cure specific areas of the outer surface of the ball. In Step 3 (FIG. 4B), the upper and lower shells (50, 51) are removed. The resulting ball (56) has an outer cover layer with pre-selected cured areas (58).

[0064] In yet another embodiment of this invention, the surface of a layer or cover or coating is first treated with a coupling agent that contains at least one free thiol-functional group. Suitable thiol containing coupling agents may include, but are not limited to, mercaptosilanes, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropyltriethoxysilane, 11-mercaptopoundecyltrimethoxysilane, mercaptomethylmethyldiethoxysilane, and 3-mercaptopropylmethyldimethoxysilane. The coupling agent may be dissolved or diluted in a suitable solvent prior to treating the surface. The coupling agent can be applied to the surface by any means including dipping, soaking, or spraying.

[0065] Once the surface has been functionalized with thiol moieties via the coupling agent, then the ene composition is applied and reacted. The ene composition may be dissolved or diluted in an appropriate solvent or used pure. The ene composition may contain a photoinitiator or thermal initiator. The thiol-ene reaction may be induced by UV or visible light, thermally, actinic radiation, or other suitable means of generating free radicals.

[0066] In yet another embodiment of this invention, the surface of a layer or cover or coating is first treated with a coupling agent that contains at least one free ene functional group. Suitable ene containing coupling agents may include, but are not limited to, acrylate and methacrylate functional

silanes, (3-acryloxypropyl)trimethoxysilane, methacryloxypropyltrimethoxysilane, N-(3-acryloxy-2-hydroxypropyl)-3-aminopropyltriethoxysilane, O-(methacryloxyethyl)-N-(triethoxy silylpropyl)urethane, N-(3-methacryloxy-2-hydroxypropyl)-3-aminopropyltriethoxysilane, methacryloxymethyltriethoxysilane, methacryloxymethyltrimethoxy silane, methacryloxypropyltriethoxysilane, (3-acryloxypropyl)methylidimethoxy silane, methacryloxymethyl)methylidimethoxysilane, (methacryloxymethyl)methylidimethoxysilane, methacryloxypropylmethylidimethoxysilane, methacryloxypropylmethylidimethoxysilane, methacryloxypropylidimethylethoxysilane, methacryloxypropylidimethylmethoxysilane, vinyl and olefin functional silanes, N-allyl-aza-2,2-dimethoxysilacyclopentane, triethoxysilylpropylmaleamic acid, allyltrimethoxysilane, 3-(N-styrylmethyl-2-aminoethylamino)propyltrimethoxysilane, vinyltriacetoxysilane, vinyltriethoxysilane, vinyltriisopropenoxysilane, vinyltriisopropoxysilane, vinyltrimethoxysilane, vinyltris(2-methoxyethoxy)silane, vinyltris(methylethylketoximino)silane, allyloxyundecyltrimethoxysilane, allyltriethoxysilane, [(bicycloheptenyl)ethyl]trimethoxysilane, norbornenyltriethoxysilane, butenyltriethoxysilane, 2-(chloromethyl)allyltrimethoxysilane, [2-(3-cyclohexenyl)ethyl]triethoxysilane, [2-(3-cyclohexenyl)ethyl]trimethoxysilane, (3-cyclopentadienylpropyl)triethoxysilane, (divinylmethylsilyl)triethoxysilane, docosenytriethoxysilane, hexadecafluorododec-11-enyl-1-trimethoxysilane, hexenyltriethoxysilane, 7-octenyltrimethoxysilane, O-(propargyloxy)-n-(triethoxysilylpropyl)urethane, styrylethyltrimethoxysilane, 10-undecenyltrimethoxysilane, o-(vinylxybutyl)-n-(triethoxysilylpropyl)urethane, vinyltri-t-butoxysilane, vinyltris(methoxypropoxy)silane, vinylmethylidimethoxysilane, vinylmethylidimethoxysilane, 1,3-divinyltetramethylsilazane, vinylidimethylethoxysilane, trivinylmethoxysilane, bis(triethoxysilyl)vinylmethylsilane, bis(triethoxysilyl)ethylene, bis(trimethoxysilyl)methyl)ethylene, 1,3-[bis(3-triethoxysilylpropyl)polyethylenoxy]-2-methylenep propane, and triethoxysilyl modified poly-1,2-butadiene.

[0067] The coupling agent maybe dissolved or diluted in a suitable solvent prior to treating the surface. The coupling agent can be applied to the surface by any means including dipping, soaking, or spraying. Once the surface has been functionalized with ene moieties via the coupling agent, then a thiol composition is applied and reacted. The thiol composition may be dissolved or diluted in an appropriate solvent or used pure. The thiol composition may contain a photoinitiator or thermal initiator. The thiol-ene reaction may be induced by UV or visible light, thermally, actinic radiation, or other suitable means of generating free radicals. In this manner, there is a layer-by-layer build-up of compositions containing thiol and ene compounds.

[0068] Inner Core Composition

[0069] In one preferred embodiment, the inner core layer (center) is made from a thermoset composition and more preferably from a thermoset rubber composition.

[0070] Suitable thermoset rubber materials that may be used to form the inner core include, but are not limited to, polybutadiene, polyisoprene, ethylene propylene rubber ("EPR"), ethylene-propylene-diene ("EPDM") rubber, styrene-butadiene rubber, styrenic block copolymer rubbers (such as "SI", "SIS", "SB", "SBS", "SIBS", and the like, where "S" is styrene, "I" is isobutylene, and "B" is butadiene), polyalkenamers such as, for example, polyoctenamer,

butyl rubber, halobutyl rubber, polystyrene elastomers, polyethylene elastomers, polyurethane elastomers, polyurea elastomers, metallocene-catalyzed elastomers and plastomers, copolymers of isobutylene and p-alkylstyrene, halogenated copolymers of isobutylene and p-alkylstyrene, copolymers of butadiene with acrylonitrile, polychloroprene, alkyl acrylate rubber, chlorinated isoprene rubber, acrylonitrile chlorinated isoprene rubber, and blends of two or more thereof. Preferably, the outer core layer is formed from a polybutadiene rubber composition.

[0071] The thermoset rubber composition may be cured using conventional curing processes. Suitable curing processes include, for example, peroxide-curing, sulfur-curing, high-energy radiation, and combinations thereof. Preferably, the rubber composition contains a free-radical initiator selected from organic peroxides, high energy radiation sources capable of generating free-radicals, and combinations thereof. In one preferred version, the rubber composition is peroxide-cured. Suitable organic peroxides include, but are not limited to, dicumyl peroxide; n-butyl-4,4-di(t-butylperoxy) valerate; 1,1-di(t-butylperoxy)3,3,5-trimethylcyclohexane; 2,5-dimethyl-2,5-di(t-butylperoxy) hexane; di-t-butyl peroxide; di-t-amyl peroxide; t-butyl cumyl peroxide; 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3; di(2-t-butyl-peroxyisopropyl)benzene; dilauroyl peroxide; dibenzoyl peroxide; t-butyl hydroperoxide; and combinations thereof. In a particular embodiment, the free radical initiator is dicumyl peroxide, including, but not limited to Perkadox® BC, commercially available from Akzo Nobel. Peroxide free-radical initiators are generally present in the rubber composition in an amount of at least 0.05 parts by weight per 100 parts of the total rubber, or an amount within the range having a lower limit of 0.05 parts or 0.1 parts or 1 part or 1.25 parts or 1.5 parts or 2.5 parts or 5 parts by weight per 100 parts of the total rubbers, and an upper limit of 2.5 parts or 3 parts or 5 parts or 6 parts or 10 parts or 15 parts by weight per 100 parts of the total rubber. Concentrations are in parts per hundred (phr) unless otherwise indicated. As used herein, the term, "parts per hundred," also known as "phr" or "pph" is defined as the number of parts by weight of a particular component present in a mixture, relative to 100 parts by weight of the polymer component. Mathematically, this can be expressed as the weight of an ingredient divided by the total weight of the polymer, multiplied by a factor of 100.

[0072] The rubber compositions may further include a reactive cross-linking co-agent. Suitable co-agents include, but are not limited to, metal salts of unsaturated carboxylic acids having from 3 to 8 carbon atoms; unsaturated vinyl compounds and polyfunctional monomers (e.g., trimethylolpropane trimethacrylate); phenylene bismaleimide; and combinations thereof. Particular examples of suitable metal salts include, but are not limited to, one or more metal salts of acrylates, diacrylates, methacrylates, and dimethacrylates, wherein the metal is selected from magnesium, calcium, zinc, aluminum, lithium, and nickel. In a particular embodiment, the co-agent is selected from zinc salts of acrylates, diacrylates, methacrylates, and dimethacrylates. In another particular embodiment, the agent is zinc diacrylate (ZDA). When the co-agent is zinc diacrylate and/or zinc dimethacrylate, the co-agent is typically included in the rubber composition in an amount within the range having a lower limit of 1 or 5 or 10 or 15 or 19 or 20 parts by weight per 100 parts of the total rubber, and an upper limit of 24 or 25 or 30 or 35 or 40 or 45 or 50 or 60 parts by weight per 100 parts of the base rubber.

[0073] Radical scavengers such as a halogenated organosulfur, organic disulfide, or inorganic disulfide compounds may be added to the rubber composition. These compounds also may function as “soft and fast agents.” As used herein, “soft and fast agent” means any compound or a blend thereof that is capable of making a core: 1) softer (having a lower compression) at a constant “coefficient of restitution” (COR); and/or 2) faster (having a higher COR at equal compression), when compared to a core equivalently prepared without a soft and fast agent. Preferred halogenated organosulfur compounds include, but are not limited to, pentachlorothiophenol (PCTP) and salts of PCTP such as zinc pentachlorothiophenol (ZnPCTP). Using PCTP and ZnPCTP in golf ball inner cores helps produce softer and faster inner cores. The PCTP and ZnPCTP compounds help increase the resiliency and the coefficient of restitution of the core. In a particular embodiment, the soft and fast agent is selected from ZnPCTP, PCTP, ditolyl disulfide, diphenyl disulfide, dixylyl disulfide, 2-nitrosorcinol, and combinations thereof.

[0074] In addition, the rubber compositions may include antioxidants. Also, processing aids such as high molecular weight organic acids and salts thereof may be added to the composition. Other ingredients such as accelerators, dyes and pigments, wetting agents, surfactants, plasticizers, coloring agents, fluorescent agents, stabilizers, softening agents, impact modifiers, antiozonants, as well as other additives known in the art may be added to the rubber composition.

[0075] The rubber composition also may include filler(s) such as materials selected from carbon black, clay and nano-clay particles as discussed above, talc (e.g., Luzenac HAR high aspect ratio talcs, commercially available from Luzenac America, Inc.), glass (e.g., glass flake, milled glass, and microglass), mica and mica-based pigments (e.g., Iridin® pearl luster pigments, commercially available from The Merck Group), and combinations thereof. Metal fillers such as, for example, particulate; powders; flakes; and fibers of copper, steel, brass, tungsten, titanium, aluminum, magnesium, molybdenum, cobalt, nickel, iron, lead, tin, zinc, barium, bismuth, bronze, silver, gold, and platinum, and alloys and combinations thereof also may be added to the rubber composition to adjust the specific gravity of the composition as needed.

[0076] Examples of commercially-available polybutadiene rubbers that can be used in accordance with this invention, include, but are not limited to, BR 01 and BR 1220, available from BST Elastomers of Bangkok, Thailand; SE BR 1220LA and SE BR1203, available from DOW Chemical Co of Midland, Mich.; BUDENE 1207, 1207s, 1208, and 1280 available from Goodyear, Inc of Akron, Ohio; BR 01, 51 and 730, available from Japan Synthetic Rubber (JSR) of Tokyo, Japan; BUNA CB 21, CB 22, CB 23, CB 24, CB 25, CB 29 MES, CB 60, CB Nd 60, CB 55 NF, CB 70 B, CB KA 8967, and CB 1221, available from Lanxess Corp. of Pittsburgh, Pa.; BR1208, available from LG Chemical of Seoul, South Korea; UBEPOL BR130B, BR150, BR150B, BR150L, BR230, BR360L, BR710, and VCR617, available from UBE Industries, Ltd. of Tokyo, Japan; EUROPRENE NEOCIS BR 60, INTENE 60 AF and P30AF, and EUROPRENE BR HV80, available from Polimeri Europa of Rome, Italy; AFDENE 50 and NEODENE BR40, BR45, BR50 and BR60, available from Karbochem (PTY) Ltd. of Bruma, South Africa; KBR 01, NdBr 40, NdBR-45, NdBr 60, KBR 7105, KBR 710H, and KBR 750, available from Kumho Petrochemical Co., Ltd. Of Seoul, South Korea; DIENE 55NF,

70AC, and 320 AC, available from Firestone Polymers of Akron, Ohio; and PBR-Nd Group II and Group III, available from Nizhnekamskneftekhim, Inc. of Nizhnekamsk, Tartarstan Republic.

[0077] The polybutadiene rubber is used in an amount of at least about 5% by weight based on total weight of composition and is generally present in an amount of about 5% to about 100%, or an amount within a range having a lower limit of 5% or 10% or 20% or 30% or 40% or 50% and an upper limit of 55% or 60% or 70% or 80% or 90% or 95% or 100%. Preferably, the concentration of polybutadiene rubber is about 40 to about 95 weight percent. If desirable, lesser amounts of other thermoset materials may be incorporated into the base rubber. Such materials include the rubbers discussed above, for example, cis-polyisoprene, trans-polyisoprene, balata, polychloroprene, polynorbornene, polyoctenamer, polypentenamer, butyl rubber, EPR, EPDM, styrenebutadiene, and the like.

[0078] As discussed above, in one preferred embodiment, a thermoset rubber composition is used to form the inner core. In alternative embodiments, the inner core layer is made from a thermoplastic material such as, for example, an ionomer composition.

[0079] Suitable ionomer compositions include partially-neutralized ionomers and highly-neutralized ionomers (HNPs), including ionomers formed from blends of two or more partially-neutralized ionomers, blends of two or more highly-neutralized ionomers, and blends of one or more partially-neutralized ionomers with one or more highly-neutralized ionomers. For purposes of the present disclosure, “HNP” refers to an acid copolymer after at least 70% of all acid groups present in the composition are neutralized.

[0080] Preferred ionomers are salts of O/X- and O/X/Y-type acid copolymers, wherein O is an α -olefin, X is a C_3 - C_5 α,β -ethylenically unsaturated carboxylic acid, and Y is a softening monomer. O is preferably selected from ethylene and propylene. X is preferably selected from methacrylic acid, acrylic acid, ethacrylic acid, crotonic acid, and itaconic acid. Methacrylic acid and acrylic acid are particularly preferred. Y is preferably selected from (meth)acrylate and alkyl (meth)acrylates wherein the alkyl groups have from 1 to 8 carbon atoms, including, but not limited to, n-butyl (meth)acrylate, isobutyl (meth)acrylate, methyl (meth)acrylate, and ethyl (meth)acrylate.

[0081] Preferred O/X and O/X/Y-type copolymers include, without limitation, ethylene acid copolymers, such as ethylene/(meth)acrylic acid, ethylene/(meth)acrylic acid/maleic anhydride, ethylene/(meth)acrylic acid/maleic acid mono-ester, ethylene/maleic acid, ethylene/maleic acid mono-ester, ethylene/(meth)acrylic acid/n-butyl (meth)acrylate, ethylene/(meth)acrylic acid/iso-butyl (meth)acrylate, ethylene/(meth)acrylic acid/methyl (meth)acrylate, ethylene/(meth)acrylic acid/ethyl (meth)acrylate terpolymers, and the like. The term, “copolymer,” as used herein, includes polymers having two types of monomers, those having three types of monomers, and those having more than three types of monomers. Preferred α , O-ethylenically unsaturated mono- or dicarboxylic acids are (meth)acrylic acid, ethacrylic acid, maleic acid, crotonic acid, fumaric acid, itaconic acid. (Meth)acrylic acid is most preferred. As used herein, “(meth)acrylic acid” means methacrylic acid and/or acrylic acid. Likewise, “(meth)acrylate” means methacrylate and/or acrylate.

[0082] In a particularly preferred version, highly neutralized E/X- and E/X/Y-type acid copolymers, wherein E is

ethylene, X is a C₃-C₅ α,β-ethylenically unsaturated carboxylic acid, and Y is a softening monomer are used. X is preferably selected from methacrylic acid, acrylic acid, ethacrylic acid, crotonic acid, and itaconic acid. Methacrylic acid and acrylic acid are particularly preferred. Y is preferably an acrylate selected from alkyl acrylates and aryl acrylates and preferably selected from (meth)acrylate and alkyl(meth)acrylates wherein the alkyl groups have from 1 to 8 carbon atoms, including, but not limited to, n-butyl (meth)acrylate, isobutyl (meth)acrylate, methyl (meth)acrylate, and ethyl (meth)acrylate. Preferred E/X/Y-type copolymers are those wherein X is (meth)acrylic acid and/or Y is selected from (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, methyl (meth)acrylate, and ethyl (meth)acrylate. More preferred E/X/Y-type copolymers are ethylene/(meth)acrylic acid/n-butyl acrylate, ethylene/(meth)acrylic acid/methyl acrylate, and ethylene/(meth)acrylic acid/ethyl acrylate.

[0083] The amount of ethylene in the acid copolymer is typically at least 15 wt. %, preferably at least 25 wt. %, more preferably at least 40 wt. %, and even more preferably at least 60 wt. %, based on total weight of the copolymer. The amount of C₃ to C₈ α,β-ethylenically unsaturated mono- or dicarboxylic acid in the acid copolymer is typically from 1 wt. % to 35 wt. %, preferably from 5 wt. % to 30 wt. %, more preferably from 5 wt. % to 25 wt. %, and even more preferably from 10 wt. % to 20 wt. %, based on total weight of the copolymer. The amount of optional softening comonomer in the acid copolymer is typically from 0 wt. % to 50 wt. %, preferably from 5 wt. % to 40 wt. %, more preferably from 10 wt. % to 35 wt. %, and even more preferably from 20 wt. % to 30 wt. %, based on total weight of the copolymer. "Low acid" and "high acid" ionomeric polymers, as well as blends of such ionomers, may be used. In general, low acid ionomers are considered to be those containing 16 wt. % or less of acid moieties, whereas high acid ionomers are considered to be those containing greater than 16 wt. % of acid moieties.

[0084] The various O/X, E/X, O/X/Y, and E/X/Y-type copolymers are at least partially neutralized with a cation source, optionally in the presence of a high molecular weight organic acid, such as those disclosed in Rajagopalan et al., U.S. Pat. No. 6,756,436, the entire disclosure of which is hereby incorporated herein by reference. The acid copolymer can be reacted with the optional high molecular weight organic acid and the cation source simultaneously, or prior to the addition of the cation source. Suitable cation sources include, but are not limited to, metal ion sources, such as compounds of alkali metals, alkaline earth metals, transition metals, and rare earth elements; ammonium salts and monoamine salts; and combinations thereof. Preferred cation sources are compounds of magnesium, sodium, potassium, cesium, calcium, barium, manganese, copper, zinc, lead, tin, aluminum, nickel, chromium, lithium, and rare earth metals. The amount of cation used in the composition is readily determined based on desired level of neutralization. As discussed above, for HNP compositions, the acid groups are neutralized to 70% or greater, preferably 70 to 100%, more preferably 90 to 100%. In one embodiment, an excess amount of neutralizing agent, that is, an amount greater than the stoichiometric amount needed to neutralize the acid groups, may be used. That is, the acid groups may be neutralized to 100% or greater, for example 110% or 120% or greater. In other embodiments, partially-neutralized compositions are prepared, wherein 10% or greater, normally 30% or greater of the acid groups are neutralized. When aluminum is used as the

cation source, it is preferably used at low levels with another cation such as zinc, sodium, or lithium, since aluminum has a dramatic effect on melt flow reduction and cannot be used alone at high levels. For example, aluminum is used to neutralize about 10% of the acid groups and sodium is added to neutralize an additional 90% of the acid groups.

[0085] "Ionic plasticizers" such as organic acids or salts of organic acids, particularly fatty acids, may be added to the ionomer resin. Such ionic plasticizers are used to make conventional ionomer composition more processable as described in the above-mentioned U.S. Pat. No. 6,756,436. In the present invention such ionic plasticizers are optional. In one preferred embodiment, a thermoplastic ionomer composition is made by neutralizing about 70 wt % or more of the acid groups without the use of any ionic plasticizer. On the other hand, in some instances, it may be desirable to add a small amount of ionic plasticizer, provided that it does not adversely affect the heat-resistance properties of the composition. For example, the ionic plasticizer may be added in an amount of about 10 to about 50 weight percent (wt. %) of the composition, more preferably 30 to 55 wt. %.

[0086] The organic acids may be aliphatic, mono- or multifunctional (saturated, unsaturated, or multi-unsaturated) organic acids. Salts of these organic acids may also be employed. Suitable fatty acid salts include, for example, metal stearates, laureates, oleates, palmitates, pelargonates, and the like. For example, fatty acid salts such as zinc stearate, calcium stearate, magnesium stearate, barium stearate, and the like can be used. The salts of fatty acids are generally fatty acids neutralized with metal ions. The metal cation salts provide the cations capable of neutralizing (at varying levels) the carboxylic acid groups of the fatty acids. Examples include the sulfate, carbonate, acetate and hydroxide salts of metals such as barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, or calcium, and blends thereof. It is preferred the organic acids and salts be relatively non-migratory (they do not bloom to the surface of the polymer under ambient temperatures) and non-volatile (they do not volatilize at temperatures required for melt-blending).

[0087] Cover Structure

[0088] The golf ball sub-assemblies of this invention may be enclosed with one or more cover layers. For example, the golf ball sub-assembly may include a core structure, and an inner cover layer may be applied over the core structure. Then, the outer cover composition comprising the multifunctional thiol and -ene compounds may be applied over the inner cover. In other versions, the golf ball sub-assembly includes the core structure and one or more casing (mantle) layers disposed about the core. An inner cover layer may be formed over the casing layer, and then the outer cover composition of the multifunctional thiol and -ene compounds may be applied.

[0089] A wide variety of thermoplastic and thermoset materials may be used in forming the inner cover composition of this invention including, for example, polyurethanes; polyureas; copolymers, blends and hybrids of polyurethane and polyurea; olefin-based copolymer ionomer resins (for example, Surlyn® ionomer resins and DuPont HPF® 1000 and HPF® 2000, commercially available from DuPont; Iotek® ionomers, commercially available from ExxonMobil Chemical Company; Amplify® 10 ionomers of ethylene acrylic acid copolymers, commercially available from Dow

Chemical Company; and Clarix® ionomer resins, commercially available from A. Schulman Inc.); polyethylene, including, for example, low density polyethylene, linear low density polyethylene, and high density polyethylene; polypropylene; rubber-toughened olefin polymers; acid copolymers, for example, poly(meth)acrylic acid, which do not become part of an ionomeric copolymer; plastomers; flexomers; styrene/butadiene/styrene block copolymers; styrene/ethylene-butylene/styrene block copolymers; dynamically vulcanized elastomers; copolymers of ethylene and vinyl acetates; copolymers of ethylene and methyl acrylates; polyvinyl chloride resins; polyamides, poly(amide-ester) elastomers, and graft copolymers of ionomer and polyamide including, for example, Pebax® thermoplastic polyether block amides, commercially available from Arkema Inc; cross-linked trans-polyisoprene and blends thereof; polyester-based thermoplastic elastomers, such as Hytrel®, commercially available from DuPont or RiteFlex®, commercially available from Ticona Engineering Polymers; polyurethane-based thermoplastic elastomers, such as Elastollan®, commercially available from BASF; synthetic or natural vulcanized rubber; and combinations thereof. Polyurethanes, polyureas, and hybrids of polyurethanes-polyureas also can be used. By the term, “hybrids of polyurethane and polyurea,” it is meant to include copolymers and blends thereof.

[0090] In one preferred embodiment, a thermoplastic ionomer composition is used to form the inner cover. Suitable thermoplastic ionomers for the inner cover may be the same ionomers used to form the core assembly as described above. Preferred ionomers are salts of O/X- and O/X/Y-type acid copolymers, wherein O is an α -olefin, X is a C_3 - C_5 α,β -ethylenically unsaturated carboxylic acid, and Y is a softening monomer. O is preferably selected from ethylene and propylene. X is preferably selected from methacrylic acid, acrylic acid, ethacrylic acid, crotonic acid, and itaconic acid. Methacrylic acid and acrylic acid are particularly preferred. Y is preferably selected from (meth)acrylate and alkyl(meth)acrylates wherein the alkyl groups have from 1 to 8 carbon atoms, including, but not limited to, n-butyl (meth)acrylate, isobutyl (meth)acrylate, methyl (meth)acrylate, and ethyl (meth)acrylate. These O/X- and O/X/Y-type acid copolymers, along with E/X and E/X/Y-type acid copolymers are described in detail above.

[0091] The inner cover layer is preferably formed from a composition comprising an ionomer or a blend of two or more ionomers that helps impart hardness to the ball. In a particular embodiment, the inner cover layer is formed from a composition comprising a high acid ionomer. A particularly suitable high acid ionomer is Surlyn 8150® (DuPont). Surlyn 8150® is a copolymer of ethylene and methacrylic acid, having an acid content of 19 wt %, which is 45% neutralized with sodium. In another particular embodiment, the inner cover layer is formed from a composition comprising a high acid ionomer and a maleic anhydride-grafted non-ionomeric polymer. A particularly suitable maleic anhydride-grafted polymer is Fusabond 525D® (DuPont). Fusabond 525D® is a maleic anhydride-grafted, metallocene-catalyzed ethylene-butene copolymer having about 0.9 wt % maleic anhydride grafted onto the copolymer. A particularly preferred blend of high acid ionomer and maleic anhydride-grafted polymer is an 84 wt %/16 wt % blend of Surlyn 8150® and Fusabond 525D®. Blends of high acid ionomers with maleic anhydride-grafted polymers are further disclosed, for example, in U.S.

Pat. Nos. 6,992,135 and 6,677,401, the entire disclosures of which are hereby incorporated herein by reference.

[0092] The inner cover layer also may be formed from a composition comprising a 50/45/5 blend of Surlyn® 8940/Surlyn® 9650/Nucrel® 960, and, in a particularly preferred embodiment, the composition has a material hardness of from 80 to 85 Shore C. In yet another version, the inner cover layer is formed from a composition comprising a 50/25/25 blend of Surlyn® 8940/Surlyn® 9650/Surlyn® 9910, preferably having a material hardness of about 90 Shore C. The inner cover layer also may be formed from a composition comprising a 50/50 blend of Surlyn® 8940/Surlyn® 9650, preferably having a material hardness of about 86 Shore C. A composition comprising a 50/50 blend of Surlyn® 8940 and Surlyn® 7940 also may be used. Surlyn® 8940 is an E/MAA copolymer in which the MAA acid groups have been partially neutralized with sodium ions. Surlyn® 9650 and Surlyn® 9910 are two different grades of E/MAA copolymer in which the MAA acid groups have been partially neutralized with zinc ions. Nucrel® 960 is an E/MAA copolymer resin nominally made with 15 wt % methacrylic acid.

[0093] The composition used to make the inner and outer covers may include fillers to adjust the specific gravity of the composition as needed. These specific-gravity adjusting fillers include high-density and low-density fillers. Suitable fillers include, for example, metal (or metal alloy) powder, metal oxides, metal stearates, particulates, carbonaceous materials, and the like, and blends thereof. Examples of useful metal (or metal alloy) powders include, but are not limited to, bismuth powder, boron powder, brass powder, bronze powder, cobalt powder, copper powder, Inconel™ metal powder, iron metal powder, molybdenum powder, nickel powder, stainless steel powder, titanium metal powder, zirconium oxide powder, aluminum flakes, tungsten metal powder, beryllium metal powder, zinc metal powder, or tin metal powder. Examples of metal oxides include, but are not limited to, zinc oxide, iron oxide, aluminum oxide, titanium dioxide, magnesium oxide, zirconium oxide, and tungsten trioxide. Examples of particulate carbonaceous materials include, but are not limited to, graphite and carbon black. Examples of other useful fillers include but are not limited to graphite fibers, precipitated hydrated silica, clay, talc, glass fibers, aramid fibers, mica, calcium metasilicate, barium sulfate, zinc sulfide, silicates, diatomaceous earth, calcium carbonate, magnesium carbonate, rubber regrind, manganese powder, and magnesium powder, cotton flock, natural bitumen, cellulose flock, and leather fiber. Other additives include, but are not limited to, optical brighteners, coloring agents, fluorescent agents, whitening agents, UV absorbers, light stabilizers, surfactants, processing aids, antioxidants, stabilizers, softening agents, fragrance components, plasticizers, impact modifiers, titanium dioxide, clay, mica, talc, ceramics, glass flakes, milled glass, ceramics, and mixtures thereof.

[0094] Golf Ball Construction

[0095] The USGA has established a maximum weight of 45.93 g (1.62 ounces) for golf balls. For play outside of USGA rules, the golf balls can be heavier. In one preferred embodiment, the weight of the multi-layered core is in the range of about 28 to about 42 grams. Also, golf balls made in accordance with this invention can be of any size, although the USGA requires that golf balls used in competition have a diameter of at least 1.68 inches. For play outside of United States Golf Association (USGA) rules, the golf balls can be of a smaller size. Normally, golf balls are manufactured in

accordance with USGA requirements and have a diameter in the range of about 1.68 to about 1.80 inches. As discussed above, the golf ball may contain a dual-layer core structure, a multi-layered cover, and also may contain intermediate (casing) layers, so the thickness levels of each of these layers also must be considered. Thus, in general, the core normally has an overall diameter within a range having a lower limit of about 1.00 or 1.20 or 1.30 or 1.40 inches and an upper limit of about 1.58 or 1.60 or 1.62 or 1.66 inches, and more preferably in the range of about 1.3 to 1.65 inches. In one embodiment, the diameter of the core sub-assembly is in the range of about 1.45 to about 1.62 inches. In turn, the casing layers (optional) and cover layers provide a ball having a diameter of at least 1.68 inches to meet USGA regulations.

[0096] It should be understood that the core structure and other layer(s) of the golf balls of this invention can be formed by any suitable technique, including injection molding, compression molding, casting, and reaction injection molding. In particular, the core sub-assembly may be formed by any conventional means including, but not limited to, compression molding, rubber-injection molding, casting of a liquid rubber, laminating, and the like.

[0097] When injection molding is used to form the core, the rubber (or other material) composition is typically in a pelletized or granulated form that can be easily fed into the throat of an injection molding machine wherein it is melted and conveyed via a screw in a heated barrel at temperatures of from 150° F. to 600° F., preferably from 200° F. to 500° F. The molten composition is ultimately injected into a closed mold cavity, which may be cooled, at ambient or at an elevated temperature, but typically the mold is cooled to a temperature of from 50° F. to 70° F. After residing in the closed mold for a time of from 1 second to 300 seconds, preferably from 20 seconds to 120 seconds, the core and/or core plus one or more additional core or cover layers is removed from the mold and either allowed to cool at ambient or reduced temperatures or is placed in a cooling fluid such as water, ice water, dry ice in a solvent, or the like.

[0098] When compression molding is used to form the core, the composition is first formed into a preform or slug of material, typically in a cylindrical or roughly spherical shape at a weight slightly greater than the desired weight of the molded core. Prior to this step, the composition may be first extruded or otherwise melted and forced through a die after which it is cut into a cylindrical preform. The preform is then placed into a compression mold cavity and compressed at a mold temperature of from 150° F. to 400° F., preferably from 250° F. to 400° F., and more preferably from 300° F. to 400° F. When compression-molding a cover layer, two half-shells of the cover layer material are first formed via injection molding. A core is then enclosed within two half-shells, which is then placed into a compression mold cavity and compressed.

[0099] In the next step, the core sub-assembly may be surface-treated to increase the adhesion between its outer surface and the next layer that will be applied over the core. Such surface-treatment may include mechanically or chemically-abrading the outer surface of the core. For example, the core may be subjected to corona-discharge, plasma-treatment, silane-dipping, or other treatment methods known to those in the art.

[0100] As discussed above, a casing layer or inner cover may be applied over the core sub-assembly prior to applying the outer cover. For example, an ethylene acid copolymer ionomer composition may be used to form an inner cover. In

one embodiment, the ionomer composition is first injection-molded to produce half-shells. The smooth-surfaced hemispherical shells are then placed around the core sub-assembly in a compression mold. Under sufficient heating and pressure, the shells fuse together to form an inner cover layer that surrounds the sub-assembly. Alternatively, the ionomer composition may be placed into a compression mold and molded under sufficient pressure, temperature, and time to produce the hemispherical shells. In another method, the ionomer composition is injection-molded directly onto the core sub-assembly using retractable pin injection molding.

[0101] The outer cover is applied over the inner cover layer. After the golf balls have been removed from the mold, they may be subjected to finishing steps such as flash-trimming, surface-treatment, marking, coating, and the like using techniques known in the art. For example, in traditional white-colored golf balls, the white-pigmented cover may be surface-treated using a suitable method such as, for example, corona, plasma, or ultraviolet (UV) light-treatment. Then, indicia such as trademarks, symbols, logos, letters, and the like may be printed on the ball's cover using pad-printing, ink-jet printing, dye-sublimation, or other suitable printing methods. Clear surface coatings (for example, primer and top-coats), which may contain a fluorescent whitening agent, are applied to the cover. The resulting golf ball has a glossy and durable surface finish.

[0102] In another finishing process, the golf balls are painted with one or more paint coatings. For example, white primer paint may be applied first to the surface of the ball and then a white top-coat of paint may be applied over the primer. Of course, the golf ball may be painted with other colors, for example, red, blue, orange, and yellow. Markings such as trademarks and logos may be applied to the painted cover of the golf ball. Finally, a clear surface coating may be applied to the cover to provide a shiny appearance and protect any logos and other markings printed on the ball.

[0103] As discussed above, the thiol-ene compositions of this invention may be used with any type of ball construction known in the art. Such golf ball designs include, for example, two-piece, three-piece, four-piece, and five-piece designs. Referring to FIG. 5, one version of a golf ball that can be made in accordance with this invention is generally indicated at (60). In this two-piece golf ball (60), the ball includes a solid, single-layered core (62) made of a suitable rubber composition such as polybutadiene rubber and a cover layer (64) made of the thiol-ene composition.

[0104] As shown in FIG. 5, when a single-layered core is used, the core preferably has a diameter within a range of about 1.40 to about 1.64 inches, preferably about 1.48 to about 1.62 inches. In FIG. 6, a three-piece ball (66) comprising a dual-core (68) having an inner core (68a) and outer core layer (68b) along with a cover (69) is shown. The inner core preferably has a diameter within a range having of about 0.70 to about 1.38 inches, preferably about 0.84 to about 1.24 inches. The outer core layer encloses the inner core such that the two-layer core preferably has an overall diameter within a range of about 1.40 to about 1.60 inches.

[0105] When a single-layered core is used, the core preferably has a center hardness within a range of about 30 to about 80 Shore C. The surface hardness of the core is preferably greater than 60 Shore C, for example, it may be in the range of about 65 to about 85 Shore C. In a particular embodiment, the surface hardness of the core is greater than the center hardness of the core to define a positive hardness gradient. In another

embodiment, the surface hardness of the core is substantially the same or less than the center hardness of the core to define a zero or negative hardness gradient. When a dual-layered core is used, the inner core (center) preferably has a geometric center hardness within a range of about 50 to about 80 Shore C. Meanwhile, the outer core layer preferably has an outer surface hardness of 70 Shore C or greater, for example 75 to 90 Shore C.

[0106] In another embodiment, as shown in FIG. 7, the four-piece golf ball (70) contains a dual-core (72) comprising an inner core (72a) and outer core layer (72b). The golf ball (70) further includes a multi-layer cover (74) comprising inner cover (74a) and outer cover (74b) layers. More particularly, in one embodiment of a four-piece ball (FIG. 7), a multi-layered cover comprising inner and outer cover layers is formed, where the inner cover layer has a thickness of about 0.01 inches to about 0.06 inches more preferably about 0.015 inches to about 0.040 inches. In this version, the inner cover layer is formed from a partially- or fully-neutralized ethylene acid copolymer ionomer having a surface hardness of greater than about 55 Shore D, more preferably greater than about 65 Shore D. In one embodiment, the inner cover has a surface hardness in the range of about 60 to about 70 Shore D. The outer cover layer, in this embodiment, preferably has a thickness of about 0.015 inches to about 0.055 inches, more preferably about 0.02 inches to about 0.04 inches. The outer cover layer preferably has a surface hardness of about 90 Shore C or less, more preferably 70 Shore C or less. For example, the outer cover may have a surface hardness in the range of about 40 to about 90 Shore C, and more preferably in the range of about 60 to about 80 Shore C. The inner cover layer is harder than the outer cover layer in this version. In another multi-layer cover embodiment, the outer cover and inner cover layer materials and thickness are the same, but the hardness range is reversed, that is, the outer cover layer is harder than the inner cover layer.

[0107] Different ball constructions can be made using the methods and core constructions of this invention as shown in FIGS. 1-7. It should be understood that the golf balls shown in FIGS. 1-7 are for illustrative purposes only, and they are not meant to be restrictive. Other golf ball constructions can be made in accordance with this invention.

[0108] For example, the thiol-ene composition of this invention is primarily discussed herein as being suitable for producing an outer cover layer for a golf ball. However, it is recognized the thiol-ene composition may be used for producing an inner core outer core layer, casing layer, cover, or any other suitable component layer for the golf ball in accordance with this invention.

[0109] In another example, the thiol-ene composition further contains a thermoset or thermoplastic material. For example, rubber materials may be blended with the thiol and ene compounds to form the polymerizable composition. These rubber compounds include, but are not limited to, polybutadiene, polyisoprene, ethylene propylene rubber ("EPR"), ethylene-propylene-diene ("EPDM") rubber, styrene-butadiene rubber, styrenic block copolymer rubbers polyalkenamers, butyl rubber, and the like.

[0110] In yet another example, thermoplastic materials may be blended with the thiol and ene compounds to form the polymerizable composition. These thermoplastic materials include the following polymers (including homopolymers, copolymers, and derivatives thereof): polyesters, polyamides, polyamide-ethers, and polyamide-esters, polyure-

thanes, polyureas, polyurethane-polyurea hybrids, fluoropolymers, polystyrenes such as poly(styrene-co-maleic anhydride), acrylonitrile-butadiene-styrene, poly(styrene sulfonate), and polyethylene styrene, polyvinyl chlorides, polycarbonates, polyethers, such as polyarylene ethers, polyimides, polyetherketones, polyamideimides, and polycarbonate/polyester copolymers.

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

We claim:

1. A golf ball having an outer coating comprising a polymerized thiol-ene composition, wherein the ball is formed by a method comprising the steps of:

- i) providing a golf ball comprising a spherical inner core and outer cover layer;
- ii) coating a polymerizable composition comprising a multifunctional thiol compound and multifunctional ene compound over the outer cover, wherein the compounds react so that a golf ball comprising a polymerized thiol-ene outer coating is formed.

2. The golf ball of claim 1, wherein the molar ratio of thiol functional groups from the thiol monomer relative to the ene functional groups from the ene monomer is about 1:1 or greater.

3. The golf ball of claim 1, wherein the molar ratio of thiol functional groups from the thiol monomer relative to the ene functional groups from the ene monomer is about 1:1 or less.

4. The golf ball of claim 1, wherein the composition further comprises a polymerization initiator selected from the group consisting of thermal initiators, photoinitiators, and mixtures thereof.

5. The golf ball of claim 4, wherein the composition further comprises a polymerization accelerator.

6. The golf ball of claim 4, wherein the composition further comprises a polymerization inhibitor.

7. The golf ball of claim 1, wherein the thiol compounds is an alkyl thiol selected from the group consisting of 1,2-dimercaptoethane, 1,6-dimercaptohexane, neopentane-tetrathiol, and the like, pentaerythritol tetra(3-mercapto propionate), 2,2-bis(mercaptomethyl)-1,3-propanedithiol, and the like, aryl thiol compounds such as 4-ethylbenzene-1,3-dithiol, 1,3-diphenylpropane-2,2-dithiol, 4,5-dimethylbenzene-1,3-dithiol, 1,3,5-benzenetrithiol, glycol dimercaptoacetate, glycol dimercaptopropionate, pentaerythritol tetrathiolglycolate, and trimethylolpropane trithiolglycolate, and mixtures thereof.

8. The golf ball of claim 1, wherein the ene compound is selected from the group consisting of tri-allyl isocyanurate; tri-vinyl isocyanurate; diallyl maleate; diallylether bisphenol A; ortho diallyl bisphenol A; triallyl trimellitate; tri(meth) acryl triols such as trimethylolpropane tri(meth)acrylate; tri-allyl triols such as 1-(allyloxy)-2,2-bis((allyloxy)methyl)butane; polyvinyl polyols such as 1-(vinylxy)-2,2-bis((vinylxy)methyl)butane; polyallyl polyols; polyvinyl polyetherpolyols; polyallyl polyetherpolyol; and mixtures thereof.

9. The golf ball of claim **1**, wherein the coating has a thickness of less than 0.005 inches.

10. A golf ball having an outer cover layer comprising a polymerized thiol-ene composition, wherein the ball is formed by a method comprising the steps of:

- i) providing a spherical inner core;
- ii) molding a polymerizable composition comprising a multifunctional thiol compound and multifunctional ene compound over the core, wherein the compounds react so that a golf ball comprising a core and polymerized thiol-ene outer cover layer is formed.

11. The golf ball of claim **10**, wherein the cover formed from the polymerizable composition is an outer cover, and the ball further comprises an inner cover, the inner cover being disposed between the inner core and outer cover.

12. The golf ball of claim **11**, wherein the inner cover is formed from an ethylene acid copolymer ionomer composition.

13. The golf ball of claim **10**, wherein the outer cover has a surface hardness in the range of about 40 to about 90 Shore C.

14. The golf ball of claim **10**, wherein the composition further comprises a polymerization initiator selected from the group consisting of thermal initiators, photoinitiators, and mixtures thereof.

15. The golf ball of claim **14**, wherein the polymerization initiator is a photoinitiator selected from the group consisting of 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophe- none; 2-hydroxy-2-methylpropiophenone; benzophenone; trimethylbenzophenone; methylbenzophenone; 1-hydroxy- cyclohexylphenyl ketone; isopropyl thioxanthone; 2,2-dimethyl-2-hydroxy-acetophenone; 2,2-dimethoxy-2-phenylac- etophenone; 2-methyl-1-[4-(methylthio)phenyl]-2- morpholino-propan-1-one; 2,4,6-trimethylbenzyl-diphenyl- phosphine oxide; 1-chloro-4-propoxythioxanthone; benzophenone; bis(2,6-dimethoxybenzoyl)-2,4,4-trimethyl pentyl phosphine oxide; 1-phenyl-2-hydroxy-2-methyl pro- panone; bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide; camphorquinone; and combinations thereof.

16. The golf ball of claim **10**, wherein the coating has a thickness of greater than 0.040 inches.

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