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(54) **GOLF BALL WITH POLYSULFIDE RUBBER LAYER**

(57) **ABSTRACT**

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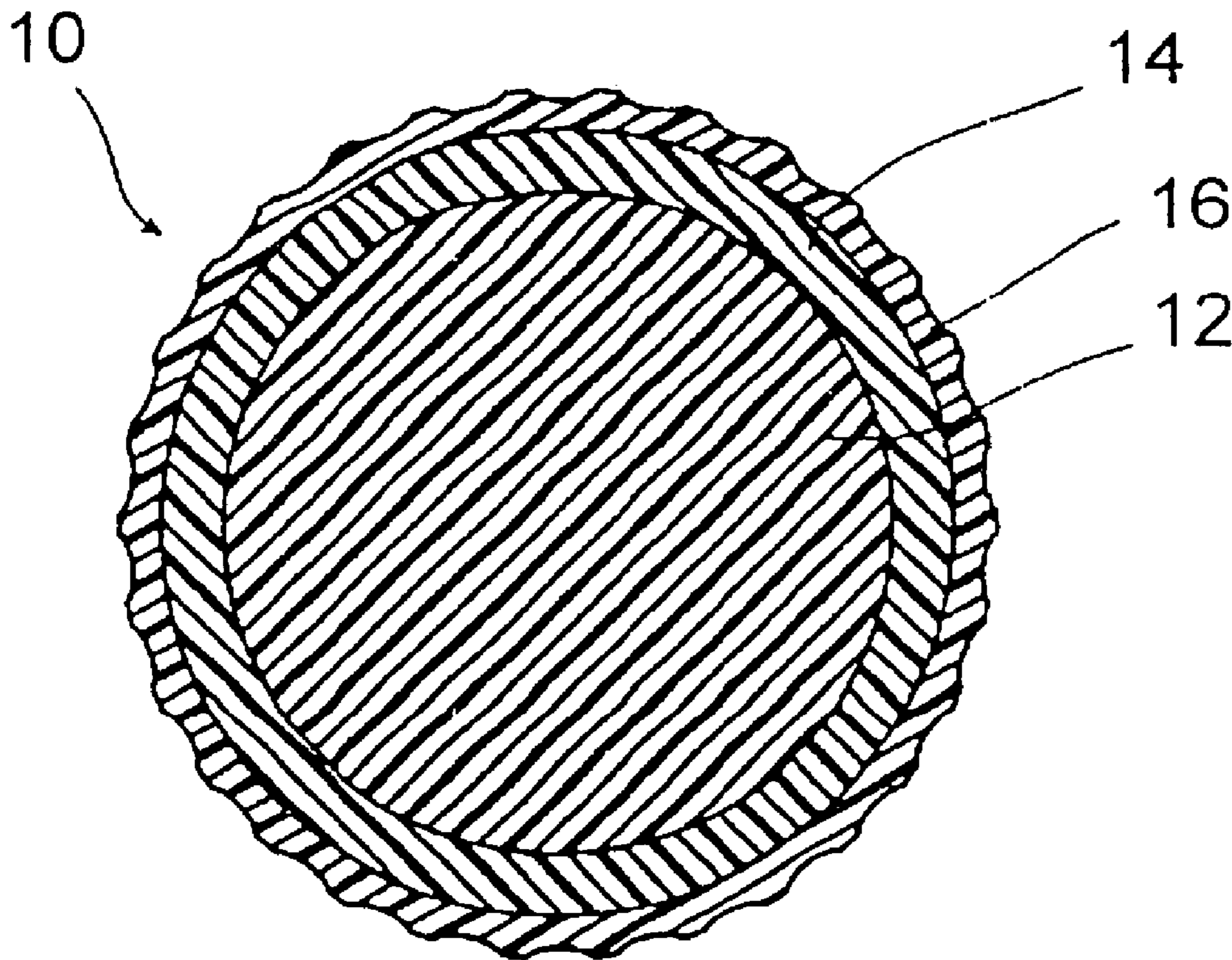
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A golf ball with at least one moisture vapor barrier layer is disclosed. In accordance to one aspect of the invention, the moisture vapor barrier layer may comprise a polysulfide rubber. Polysulfide rubber may be applied to the golf ball in a liquid form curable at an elevated temperature or at room temperature. The liquid form may be mixed from two or more components prior to being applied to the ball. The liquid form may have water mixed therein before being applied to the ball. Alternatively, the liquid form may be applied to the ball without any additional mixing.

The polysulfide rubber may be formed from a solid form that has been heated to a flowable condition and extruded or cast to form the moisture vapor barrier layer. The polysulfide rubber may be dissolved in a solvent and applied to the ball, wherein the solvent is allowed to evaporate or otherwise flashed.

The present invention is also directed to a golf ball comprising a layer of moisture vapor barrier with a moisture vapor transmission rate preferably lower than that of the cover. Preferably, the moisture vapor barrier layer comprises a material curable at room temperature. Preferably the moisture vapor barrier layer is a polysulfide rubber that is curable at room temperature.



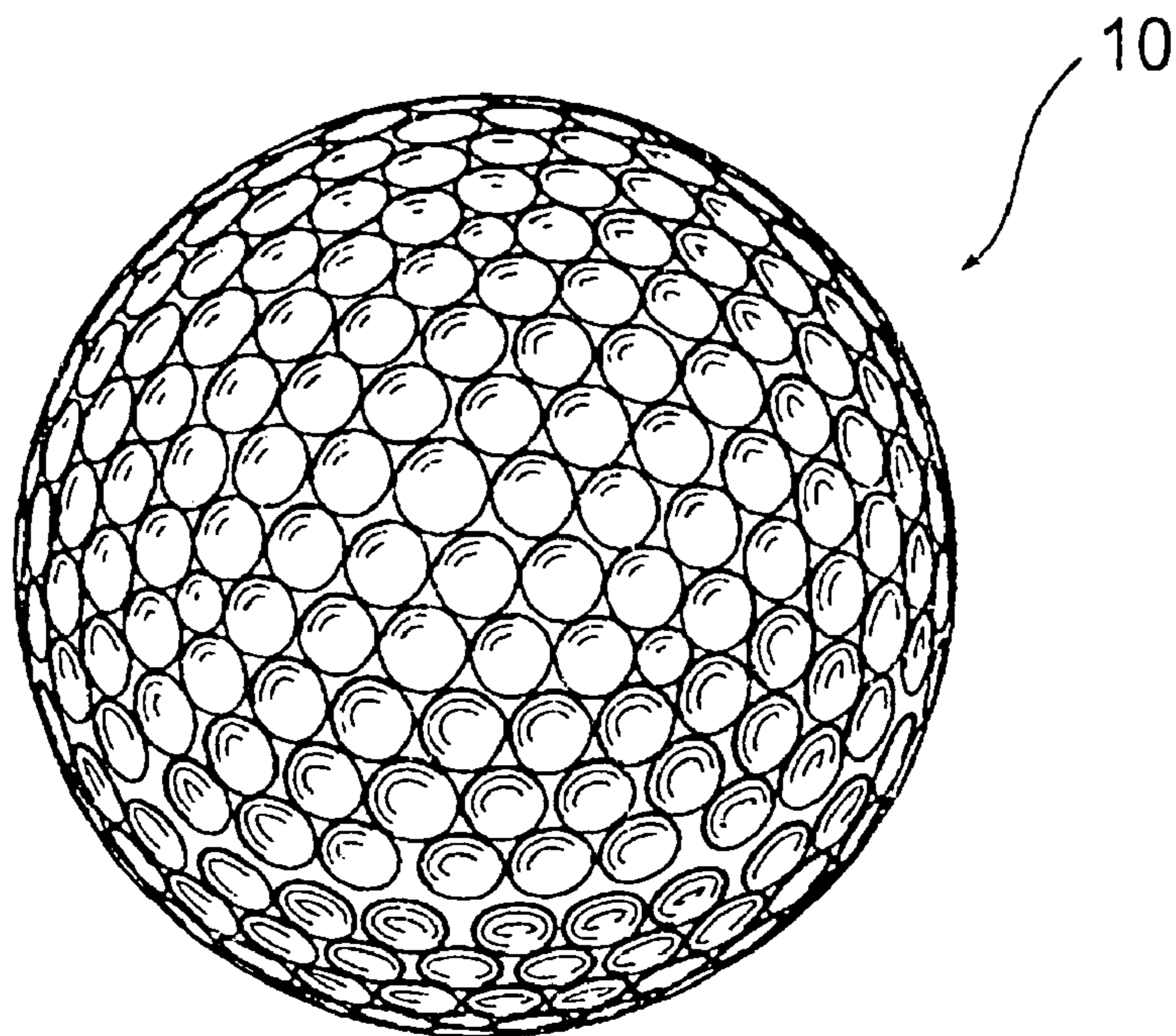


FIG. 1

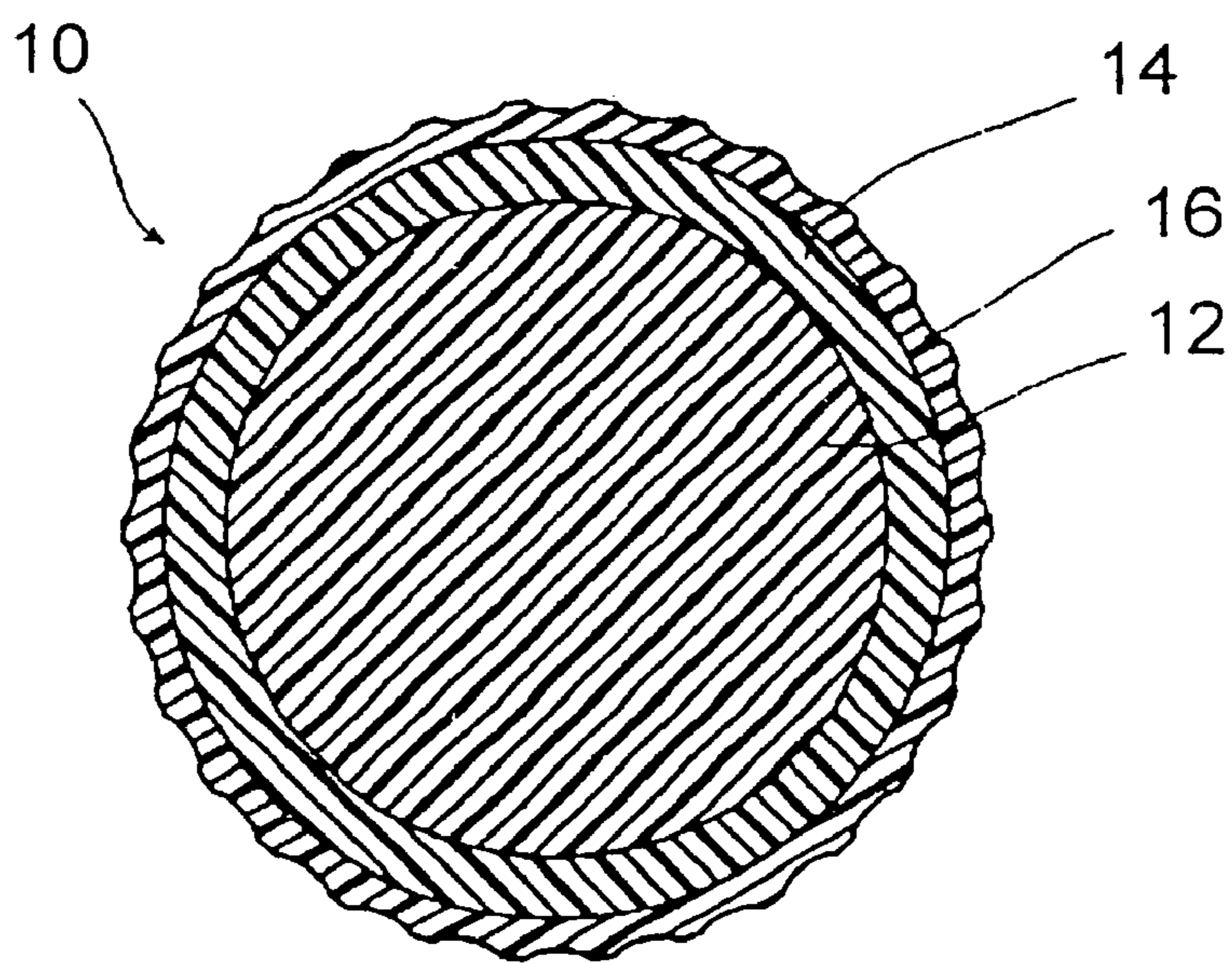


FIG. 2

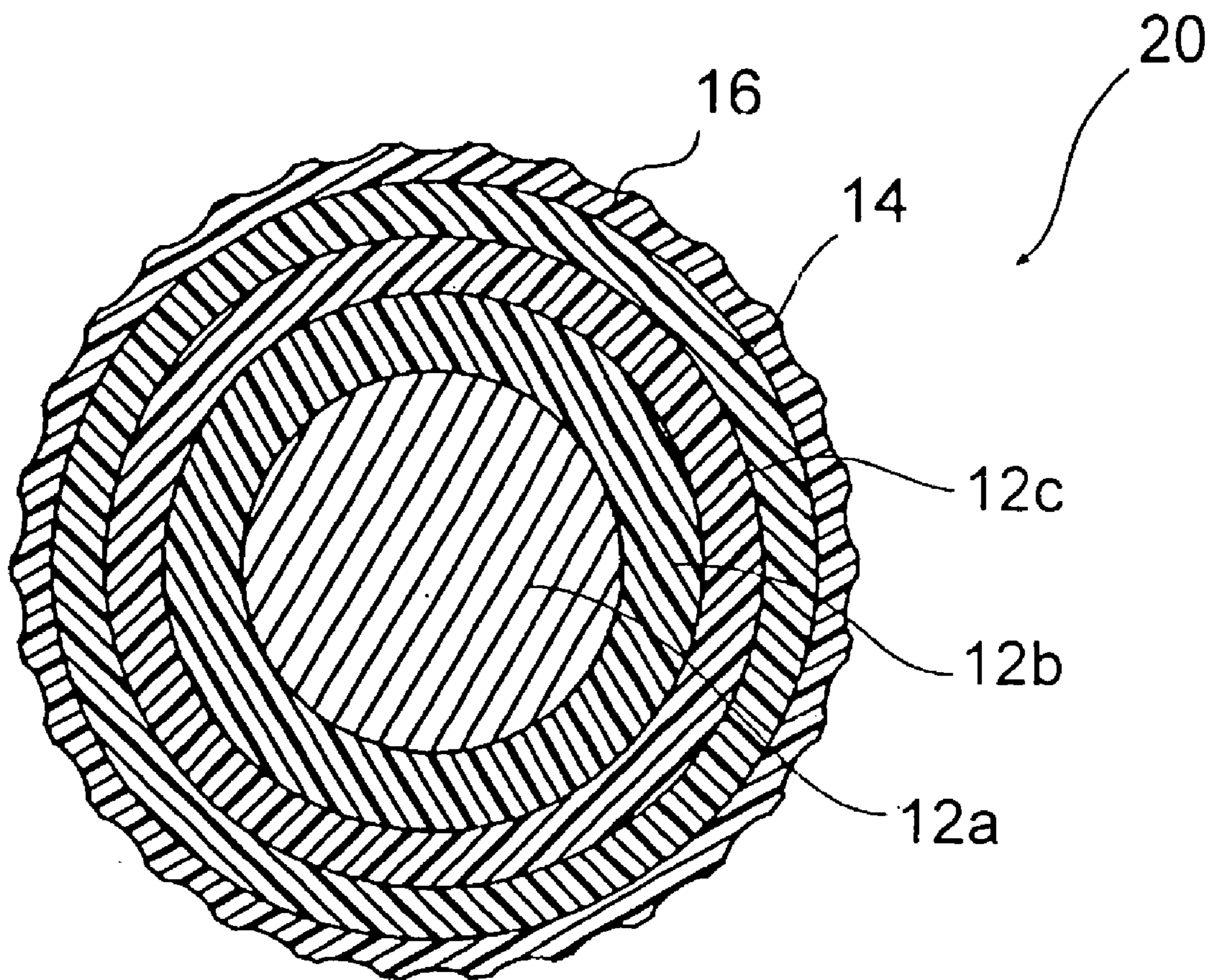


FIG. 3

GOLF BALL WITH POLYSULFIDE RUBBER LAYER

STATEMENT OF RELATED PATENT APPLICATION

[0001] This non-provisional utility patent application is a continuation of co-pending U.S. patent application bearing Ser. No. 10/103,413, filed on Mar. 21, 2002, which is a continuation-in-part of U.S. patent application bearing Ser. No. 09/973,342, filed on Oct. 9, 2001, now U.S. Pat. No. 6,632,147. The parent application and patent are hereby incorporated by reference in their entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to a novel structure for a golf ball, and more particularly to a golf ball with a moisture vapor barrier layer.

BACKGROUND OF THE INVENTION

[0003] Solid core golf balls are well known in the art. Typically, the core is made from polybutadiene rubber material, which provides the primary source of resiliency for the golf ball. U.S. Pat. No. 3,241,834 and U.S. Pat. No. 3,313,545 disclose the early work in polybutadiene chemistry. It is also known in the art that increasing the cross-link density of polybutadiene can increase the resiliency of the core. The core is typically protected by a cover from repeated impacts from golf clubs. The golf ball may comprise additional layers, which can be an outer core or an inner cover layer. One or more of these additional layers may be a wound layer of stretched elastic windings to increase the ball's resiliency.

[0004] A known drawback of polybutadiene cores cross-linked with peroxide and/or zinc diacrylate is that this material is adversely affected by moisture. Water moisture vapor reduces the resiliency of the cores and degrades its properties. A polybutadiene core will absorb water and lose its resiliency. Thus, these cores must be covered quickly to maintain optimum ball properties. The cover is typically made from ionomer resins, balata, and urethane, among other materials. The ionomer covers, particularly the harder ionomers, offer some protection against the penetration of water vapor. However, it is more difficult to control or impart spin to balls with hard covers. Conventional urethane covers, on the other hand, while providing better ball control, offer less resistance to water vapor than ionomer covers.

[0005] Prolonged exposure to high humidity and elevated temperature may be sufficient to allow water vapor to invade the cores of some commercially available golf balls. For example at 110° F. and 90% humidity for a sixty day period, significant amounts of moisture enter the cores and reduce the initial velocity of the balls by 1.8 ft/s to 4.0 ft/s or greater. The change in compression may vary from 5 PGA to about 10 PGA or greater. The absorbed water vapor also reduces the coefficient of restitution (COR) of the ball.

[0006] Several prior patents have addressed the water vapor absorption problem. U.S. Pat. No. 5,820,488 discloses a golf ball with a solid inner core, an outer core and a water vapor barrier layer disposed therebetween. The water vapor barrier layer preferably has a water vapor transmission rate lower than that of the cover layer. The water vapor barrier

layer can be a polyvinylidene chloride (PVDC) layer. It can also be formed by an in situ reaction between a barrier-forming material and the outer surface of the core. Alternatively, the water vapor barrier layer can be a vermiculite layer. U.S. Pat. No. 5,885,172 and U.S. Pat. No. 6,132,324 disclose, among other things, a golf ball with a polybutadiene or wound core with an ionomer resin inner cover and a relatively soft outer cover. The hard ionomer inner cover offers some resistance to water vapor penetration and the soft outer cover provides the desirable ball control. Additionally, U.S. Pat. No. 5,875,891 discloses an impermeable packaging for golf balls. The impermeable packaging acts as a moisture barrier limiting moisture absorption by golf balls during storage, but not during use.

[0007] The moisture vapor barrier layer disclosed in the prior patents can be rigid and makes the ball stiffer. Furthermore, producing a rigid layer may cause significant production obstacles. On the other hand, polysulfide rubber is known in the extrusion art, the sealant art, and related arts as a soft polymer with excellent water barrier property, as discussed in U.S. Pat. No. 6,322,650 B1, U.S. Pat. No. 4,263,078, U.S. Pat. No. 4,165,425 and U.S. Pat. No. 4,190,625. These references are incorporated herein by reference in their entireties. Polysulfide rubber, however, has not heretofore been appreciated in the golf ball art. The prior golf ball patents that disclose water moisture barrier layers do not mention polysulfide rubber as a suitable barrier material. The golf ball patents that mention polysulfide rubber, however, do not discuss its water barrier property. For example, U.S. Pat. No. 3,940,145 suggests that the core could be made from a solid damping material, such as polysulfide. U.S. Pat. No. 4,429,068 discloses a rubber compound that may include polysulfide rubber among more voluminous ingredients for use in automobile tires and possibly in golf ball cores. U.S. Pat. No. 6,187,864 B1 discloses a golf ball comprising a core, a cover and optional intermediate layers. When an intermediate layer is made from a compatibilizer-free blend of an ionomer and a polyamide polymer, then the cover may be made from a material selected from a group of non-ionomers and non-olefin ionomers, wherein one of the non-ionomers is polysulfide rubber.

[0008] Hence, there remains a need for a golf ball with an improved water vapor barrier layer and improved methods for applying a water vapor barrier layer on to the core of the golf ball.

SUMMARY OF THE INVENTION

[0009] The present invention is directed to a golf ball comprising a layer of moisture vapor barrier with a moisture vapor transmission rate preferably lower than that of the cover. Preferably, the moisture vapor barrier layer comprises a polysulfide rubber.

[0010] Polysulfide rubber may be applied to the golf ball in a liquid form curable at an elevated temperature or at room temperature. The liquid form may be mixed from two or more components prior to being applied to the ball. The liquid form may have water mixed therein before being applied to the ball. Alternatively, the liquid form may be applied to the ball without any mixing.

[0011] The polysulfide rubber may be formed from a solid that has been heated to a flowable condition, and extruded or

cast to form the moisture vapor barrier layer. The polysulfide rubber may be dissolved in a solvent and applied to the ball, wherein the solvent is allowed to evaporate or otherwise flashed.

[0012] The present invention is also directed to a golf ball comprising a layer of moisture vapor barrier with a moisture vapor transmission rate preferably lower than that of the cover. Preferably, the moisture vapor barrier layer comprises a material curable at room temperature. Preferably the moisture vapor barrier layer is a polysulfide rubber that is curable at room temperature.

[0013] The present invention is also directed to a golf ball comprising a soft, high specific gravity layer. Preferably, this layer also has a low moisture vapor transmission rate to decrease the amount of moisture penetrating into the core of the golf ball. The high specific gravity layer advantageously contributes to a high moment of inertia, low driver spin ball.

[0014] In accordance to another aspect of the invention, the moisture vapor barrier can be an intermediate layer, an inner cover layer, an outer core layer, a core coating or an outer cover coating. The present invention is also directed to a golf ball having a thin moisture vapor barrier layer with a thin, soft thermoset urethane cover.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] In the accompanying drawings which form a part of the specification and are to be read in conjunction therewith and in which like reference numerals are used to indicate like parts in the various views:

[0016] **FIG. 1** is a front view of a dimpled golf ball in accordance to the present invention;

[0017] **FIG. 2** is a cross-sectional view of the golf ball in **FIG. 1** showing a solid core surrounded by a thin moisture vapor barrier layer and a cover; and

[0018] **FIG. 3** is a cross-sectional view of another golf ball in accordance to the present invention showing a solid core with multiple wound layers surrounded by a thin moisture vapor barrier layer.

DETAILED DESCRIPTION OF THE INVENTION

[0019] As shown generally in **FIGS. 1 and 2**, where like numbers designate like parts, reference number **10** broadly designates a golf ball in accordance to the present invention. Golf ball **10** preferably has a solid core **12**, an intermediate layer **14** and a cover **16**. Solid core **12** may comprise a single spherical element, or it may comprise a core spherical element with one or more intermediate layers surrounding the spherical element. Solid core **12** can be made from any suitable core materials including thermoset plastics, such as natural rubber, polybutadiene (PBD), polyisoprene, styrene-butadiene or styrene-propylene-diene rubber, and thermoplastics such as ionomer resins, polyamides, polyesters, or a thermoplastic elastomer. Suitable thermoplastic elastomers include Pebax®, which is believed to comprise polyether amide copolymers, Hytrel®, which is believed to comprise polyether ester copolymers, thermoplastic urethane, and Kraton®, which is believed to comprise styrenic block copolymers elastomers. These products are commercially available from Elf-Atochem, E.I. Du Pont de Nemours and

Company, various manufacturers, and Shell Chemical Company, respectively. The core materials can also be formed from a castable material. Suitable castable materials include those comprising a urethane, polyurea, epoxy, silicone, IPN's, etc.

[0020] Additionally, suitable core materials may also include a reaction injection molded polyurethane or polyurea, including those versions referred to as nucleated, where a gas, typically nitrogen, is essentially whipped into at least one component of the polyurethane, typically, the pre-polymer, prior to component injection into a closed mold where essentially full reaction takes place resulting in a cured polymer having reduced specific gravity. These materials are referred to as reaction injection molded (RIM) materials. Alternatively, the core may have a liquid center.

[0021] Cover **16** is preferably tough, cut-resistant, and selected from conventional materials used as golf ball covers based on the desired performance characteristics. The cover may comprise one or more layers. Suitable cover materials include ionomer resins, such as Surlyn® available from DuPont, blends of ionomer resins, thermoplastic or thermoset urethane, acrylic acid, methacrylic acid, thermoplastic rubber polymers consisting of block copolymers in which the elastomeric midblock of the molecule is an unsaturated rubber or a saturated olefin rubber, e.g., Kraton® rubbers available from Shell Chemical Co., polyethylene, and synthetic or natural vulcanized rubber such as balata.

[0022] Additionally, other suitable core and cover materials are disclosed in U.S. Pat. No. 5,919,100 and international publications WO 00/23519 and WO 01/29129. These disclosures are incorporated by reference in their entirety. Preferably, core **12** is made from a polybutadiene rubber material and cover **16** is made from a composition comprising a thermoset or thermoplastic urethane or a composition comprising an ionomer resin.

[0023] To prevent or minimize the penetration of moisture, typically water vapor, into core **12** of golf ball **10**, intermediate layer **14** is a moisture vapor barrier layer preferably disposed around core **12**. Preferably, moisture vapor barrier layer **14** has a moisture vapor transmission rate that is lower than that of the cover, and more preferably less than the moisture vapor transmission rate of an ionomer resin such as Surlyn®, which is in the range of about 0.45 to about 0.95 grams-mm/m²·day. The moisture vapor transmission rate is defined as the mass of moisture vapor that diffuses into a material of a given thickness per unit area per unit time. The preferred standards of measuring the moisture vapor transmission rate include ASTM F1249-90 entitled "Standard Test Method for Water Vapor Transmission Rate Through Plastic Film and Sheeting Using a Modulated Infrared Sensor," and ASTM F372-94 entitled "Standard Test Method for Water Vapor Transmission Rate of Flexible Barrier Materials Using an Infrared Detection Technique," among others.

[0024] A preferred material suitable for the water vapor barrier layer is polysulfide rubber. Polysulfide rubber typically has a high sulphur content, which makes the material resistant to hydrocarbons, gasoline, diluted acids, alkaline, water, alcohol, acetone, esters, among other things. Polysulfide is also highly resistant to diffusion of gases. In accordance to one estimate, polysulfide is 40 times less permeable to vapor than natural rubber. The water vapor transmission

rate for polysulfide is typically in the range of about 0.01 grams·mm/m²·day to about 0.50 grams·mm/m²·day. The water vapor transmission rate depends on the particular composition of the polysulfide compound, including functionality, molecular weight, curatives and fillers, among other things. For example, an isocyanate functionalized polysulfide generally has higher water vapor transmission rate and a relatively purer, high molecular weight polysulfide generally has lower water vapor transmission rate.

[0025] Advantageously, polysulfide has a specific gravity in the range of about 1.2 to 1.3, so that this material can also be used to alter the ball's moment of inertia. Polysulfide may have specific gravity of greater than 1.3, greater than 1.5, or greater than 2.0 when high specific weight fillers, flakes, fibers, particulates or other additives are added. As a cured solid, it is also capable of being elongated to about 400%-500% prior to breakage. This property helps prevent breakage when the material is being made into a golf ball layer.

[0026] Polysulfide rubber typically is available in three forms: a millable, extrudable solid elastomer that exhibits thermoplastic properties, a dispersion of high molecular weight polymer in solvents, or a liquid polymer. In the liquid form, polysulfide rubber is a low molecular weight liquid that cures to form an elastomeric sealant. The liquid form is often available in two or more components that are mixed together to cause a reaction to cure or vulcanize the components into an elastic sealant. The liquid form is also available as a single component that cures at an elevated temperature. It is also available as a single component that cures when exposed to water vapor in the ambient atmosphere at ambient temperature.

[0027] In the solid form, polysulfide rubber is a cured or vulcanized rubber capable of flow under pressure and elevated temperature with substantial recovery of its preflow physical properties upon cooling. As the solid polymer is heated to the flowable state, the polysulfide rubber can be extruded or it can be cast into a mold to form a moisture vapor barrier layer for golf ball **10**.

[0028] Polysulfide rubber is also available dissolved in a solvent, such as aliphatic and aromatic hydrocarbons, esters, ketones and alcohols, among others. Solvents are typically used to reduce the viscosity of liquid polysulfide to apply the polysulfide as a thin film of water vapor barrier layer on the golf ball. The solvent is allowed to evaporate or otherwise flashed before the cover layer **16** is cased thereon. The advantages of a solvent-based polysulfide rubber are that the water vapor barrier can be formed by dipping or spraying and that no precise mixing of the multiple components is required.

[0029] The chemical compositions and the reactions necessary to produce polysulfide rubber are well known and are fully described in U.S. Pat. Nos. 2,195,380, 2,466,963 and U.S. Pat. No. 3,243,403 among others. The disclosures of these patents are incorporated herein by reference in their entireties. In general, polysulfide rubbers are synthetic polymers prepared by reacting polyfunctional organic compounds with alkali metal or alkaline earth metal sulfide solutions to provide high molecular weight polymers having the recurring unit, RSS, wherein R is typically a divalent organic radical and SS is a disulfide linkage through which the organic radicals are interconnected. To improve the properties of the polysulfide polymers, a mixture of difunc-

tional and trifunctional organic compounds is typically used. The trifunctional compound is present at a relatively small amount to produce a slightly cross-linked structure. The organic radicals typically include aliphatic halides, e.g., alkylene chlorides, such as ethylene dichloride and its homologues, or oxygen-containing aliphatic dichloride such as bis-beta-chloroethyl ether and bio-beta-chloroethyl formal.

[0030] The liquid form of polysulfide rubber, as described in the '963 and '403 patents, is obtained by splitting high molecular weight polymers described in the preceding paragraph to form polythiopolymercaptan polymers having molecular weights on the order of 500 to 25,000 and having viscosities in the range of 300 to 100,000 centipoises. The liquid form can be cured by a variety of curing agents, including those disclosed in U.S. Pat. No. 2,466,963. The cured materials, e.g., solid elastomers, have excellent resistance to hydrocarbons, water, acids, alkalis and atmospheric oxidation. Hence, the cured solid elastomers are very useful as sealants and impermeable lining materials, and as disclosed herein, cured polysulfide rubber is utilized to protect a golf ball core, particularly a core comprising polybutadiene, against water vapor encroachment.

[0031] Examples of suitable liquid polysulfide rubbers include those prepared from bis-beta-chloroethyl formal and are essentially composed of recurring (S·CH₂·CH₂·O·CH₂·O·CH₂·CH₂·S) groups and have free mercapto terminals through which the liquid may be cured. Typically, a small percentage of trichloropropane is mixed with the bis-beta-chloroethyl formal to provide the cross-linking. Suitable curing agents include an oxidizing agent such as zinc peroxide, lead peroxide or the curing agents disclosed in the '963 patent. Other non-toxic curing agents are disclosed in U.S. Pat. No. 3,046,248, which is incorporated herein by reference. Modifying agents, such as cure-retarding agents, cure accelerating agents, pigments, fillers may be incorporated into the composition. By selecting the proper curing agents and modifying agents, cures at room temperature can be achieved. On the other hand, cures at elevated temperature can be used to reduce the overall curing time. Cures may also be accelerated in the presence of acid, and retarded under alkaline conditions, when dibutyl tin oxide is used as a curing agent. On the other hand, when other curing agents are used, cures may be retarded under acidic conditions and accelerated under alkaline conditions. Typically, the liquid base polymer and the curing agent(s) are mixed just prior to use. It is also possible to premix the liquid base polymer and the curing agent(s) under anhydrous conditions, and immediately before use water is added to the premixed condition to cure the polymer.

[0032] Liquid polysulfide polymers are also available in a single component or a one-part stable, hygroscopic liquid polymer that cures when it contacts moisture in atmospheric air without the need of curing agent(s) or water. Examples of such one-part liquid polymer include a liquid polyalkylene polysulfide polymer. Dispersed in such liquid are a dormant curing agent that is activated by the presence of moisture, and a water-soluble deliquescent accelerating agent adapted to attract and absorb moisture from the surrounding. Such one-part curable polymer is disclosed in U.S. Pat. No. 3,225,017, and the disclosure of this patent is hereby incorporated by reference in its entirety. The one-part curable polymer may be initially dried to remove moisture.

Alternatively, the deliquescent accelerating agent may also be a desiccating agent to dry the polymer. Alternatively, a single additive can be desiccating, deliquescent, dormant curing and accelerating agent dispersed to dry the polymer and to cure the polymer when exposed to moisture. Suitable curing agents for the one-part curable polymers include organic oxidizing agents, such as dinitro benzene, and inorganic oxides, such as alkali metal and alkali metal salt peroxide (e.g., sodium peroxide, sodium pyrophosphate peroxide, sodium carbonate peroxide and sodium perborate), the alkali earth metal peroxides (e.g., calcium peroxide and barium peroxide), and other metal peroxides such as zinc peroxide and manganese dioxide and oxidizing agents (e.g. ammonium dichromate).

[0033] As disclosed in the '017 patent, suitable deliquescent accelerating agents, which are also desiccant and water-soluble, include alkaline materials such as alkali metal, alkaline earth metal oxides, peroxides, hydroxides and salts of weak acids. Examples of such agents include barium oxide, sodium oxide, sodium peroxide, potassium hydroxide, sodium hydroxide, sodium acetate, sodium carbonate, sodium phosphate, sodium molybdate, calcium oxide, barium oxide, calcium peroxide, barium peroxide, calcium hydroxide and strontium hydroxide. A more preferred agent is barium oxide, due to its effectiveness as a desiccating deliquescent accelerating agent. More specifically, sodium peroxide, calcium peroxide and barium peroxide are suitable as single desiccating, deliquescent accelerating agent. In a particular example, where a one-part liquid polymer, i.e., polyalkylene polysulfide, has a molecular weight of about 4,000, the curing agent should be about 2 to 20 parts per 100 parts of polyalkylene polysulfide, and 0.5 to 50 parts of desiccating, deliquescent accelerating agent.

[0034] Another example of a curable liquid polysulfide polymer at room temperature by atmospheric moisture with or without additional curing agents or catalysts is an isocyanate-terminated polysulfide polymer, disclosed in U.S. Pat. No. 3,386,963, which is incorporated herein by reference.

[0035] Another example of water vapor barrier material based on an isocyanate-terminated liquid polysulfide polymer is disclosed in U.S. Pat. No. 6,322,650 B1. This liquid polymer is formed by first splitting the polysulfide by reacting it as a latex dispersion in water with a dithiodialkylene glycol and aqueous sodium sulfite at the reflux temperature and adding hydrogen peroxide for oxidative coupling of chains having residual mercaptan groups. This reaction yields hydroxyl-terminated polysulfide having a molecular weight of about 3% of the pre-reaction value, or about 2500 to 4000. The water vapor barrier material is then prepared by reacting the hydroxyl terminated polysulfide with a polyisocyanate at a ratio between 1::1 and 1::1.2 on an equivalent basis. Generally, any organic polyisocyanate is suitable, including isophorone diisocyanate (abbreviated as IPDI); arylene polyisocyanates such as tolylene-, metaphenylene-, methylene-bis-(phenylene-4-) (abbreviated as MDI and sold under the trademark RUBINATE 9310), biphenylene-4,4'-; 3,3'-dimethoxybiphenylene-4,4'-; 3,3'-biphenylene-4,4'-; and methylene-(tetramethylxylene-) (abbreviated as MTMXDI); alkylene polyisocyanates such as ethylene-, ethylidene-, propylene-1,2-, butylene-1,4-; butylene-1,3-; cyclohexylene-1,4-; methylene-bis(cyclohexyl-4,4')-; and hexamethylene-1,6-diisocyanate (abbreviated as HDI). Additives, such as a curing catalyst, a chain stopper, a

plasticizer, fillers, dehydrating agents and thixotropic agents can be added to the reaction. This water vapor barrier material or sealant exhibits very low moisture vapor transmission rate.

[0036] Another example of a liquid polysulfide polymer curable at room temperature relatively quickly (less than 1 hour at about 70-75° F.) is disclosed in U.S. Pat. No. 3,637,574. This is achieved by a composition comprising a tetraalkylthiuram polysulfide, inorganic metal curing agent (e.g., zinc peroxide or zinc oxide) and elemental sulfur. After the components are mixed and homogenized, the composition is curable in the ambient atmosphere at room temperature. The '574 patent is incorporated herein by reference in its entirety.

[0037] As stated above, polysulfide polymers are also available in solid form. Examples of solid, extrudable and castable polysulfide rubbers are disclosed in U.S. Pat. Nos. 4,263,078, 4,165,425 and U.S. Pat. No. 4,190,625 among others. These references have been incorporated by reference. The '625 patent discloses a thermoplastic, elastomeric polysulfide rubber that can be extruded or cast. This polysulfide rubber is a hydroxyl terminated rubber cured by a zinc oxide. It also has sulfur linkages averaging about at least 1.8 sulfur atoms per linkage unit and is catalyzed by an alkali metal hydroxide. The catalytic agent induces softening on heating and helps the elastomer to regain its pre-heating properties upon cooling. The extrusion of this polysulfide rubber is accomplished using standard equipment suitable for extruding other solid thermoplastic elastomers.

[0038] In another example, the solid polysulfide rubber is cured with lower alkyl tin oxide, such as di-n-butyl tin oxide, and used in hot applied processes as disclosed in the '425 patent. This particular polysulfide rubber is thiol terminated and cured with the lower alkyl tin oxide at temperatures between 100° C. and 300° C. to become a solid thermoplastic elastomer that can be softened by heating and then cast or injection molded into a water vapor barrier layer.

[0039] Another suitable solid polysulfide rubber is based on another thiol terminated liquid polysulfide polymer cured with zinc oxide and a sulfur containing compound selected from 2-mercaptobenzothiazol, zinc lower alkyl dithiocarbamate and alkyl thiuram polysulfides at temperatures from about 200° F. to about 390° F. Agents, which improve the flowing properties of the composition, such as copolymers of styrene and alkylenes, organic or inorganic reinforcing fibrous materials, phenolic resins, coumarone-indene resins, antioxidants, heat stabilizers, polyalkylene polymers, factice, terpene resins, terpene resins esters, benzothiazyl disulfide or diphenyl guanidine, can also be added to the composition. Advantageously, this polysulfide rubber possesses a good ability to wet the substrate and forms good bonds with such substrate when cooled and, therefore, is one preferred sealant for the golf ball core.

[0040] Preferably, a golf ball in accordance to the present invention comprises a solid or multiple-layer solid core **12** having an outer diameter of greater than about 1.50 inches, more preferably 1.550 inches and most preferably about 1.580 inches. Moisture vapor barrier layer **14** has a thickness preferably in the range of about 0.001 inch to about 0.100 inch, more preferably in range of about 0.010 inch to about 0.050 inch and cover **16** is a urethane cover with sufficient thickness to produce a 1.680 inch diameter golf ball.

[0041] In accordance to one aspect of the invention, the Shore D hardness values for the core and moisture vapor barrier sub-assemblies have been measured less than about 60 and more specifically in the range of about 30-50. Alternatively, according to other aspects of the invention, the moisture barrier sub-assemblies may have Shore D hardness value of greater than 50, when more rigid materials, such as stiff ionomer with a Shore D hardness of greater than 55 are used in conjunction with the moisture vapor barrier layer 14.

[0042] In accordance to a preferred embodiment of the invention, a golf ball with a solid PBD core with the thin moisture barrier layer, discussed immediately above, is covered by a thermoset urethane cover having a thickness from about 0.010 to about 0.050 inch, more preferably about 0.030 inch and has a Shore D of less than 65, more preferably less than 50 and even more preferably in the range of about 30 to about 40.

[0043] In accordance to yet another aspect of the invention, as shown in FIG. 3 golf ball 20 may have multiple layer core 12a, 12b and 12c, surrounded by intermediate layer 14 and dimpled cover 16. Core layers 12b and 12c may be an integral solid layer or discrete layers molded on each other. Alternatively, both outer core layers 12b and 12c could be wound layers, or one of these two layers may be a wound layer, and the innermost core 12a may be liquid-filled.

[0044] Advantageously, the intermediate moisture vapor barrier layer 14, preferably a polysulfide rubber dissolved in solvent or a liquid one-component or multiple-component polysulfide, may surround one or both of the wound layers 12b and 12c to minimize moisture from penetrating into the innermost core 12a and the wound layers, especially when one or both of the wound layers or the innermost core are made from a rubber or polybutadiene material or from other materials that are degradable by moisture.

[0045] In accordance to another aspect of the invention, the moisture vapor barrier layer 14 may be made by a number of methods. Non-limiting examples include, but are not limited to, the following methods:

[0046] (i) Pre-formed semi-cured shells. A quantity of mixed stock of the solid polysulfide rubber in extrudable form is placed into a compression mold and molded under sufficient pressure, temperature and time to produce semi-cured, semi-rigid half-shells. The half-shells are then placed around a core (solid or wound) and the sub-assembly is cured in another compression molding machine to complete the curing process and to reach the desirable size. A cover is then formed on the sub-assembly by any known method to complete the fabrication of the ball.

[0047] (ii) Sheet stock and vacuum. Thin sheets of the solid polysulfide rubber are placed on the upper and lower platens of a compression-molded press. Suction force from a vacuum keeps the sheets tight against the mold cavities. A core (solid or wound) is placed in the bottom cavity above the vacuumed sheet. The sub-assembly is then cured in a compression molding press to cure the sub-assembly and to achieve the desirable size. A cover is then formed on the sub-assembly by any known method to complete the fabrication of the ball.

[0048] (iii) Rubber injection molding. Stock of the solid polysulfide rubber in extrudable form is fed into an injection molding barrel and screw. The stock is then injected through a nozzle into a mold cavity and surrounds a core (solid or wound). The sub-assembly is then heated under pressure to cure the sub-assembly and to achieve the desirable size. A cover is then formed on the sub-assembly by any known method to complete the fabrication of the ball.

[0049] Other suitable manufacturing techniques include spraying, dipping, vacuum deposition, reaction injection molding, among others. The moisture vapor barrier layer 14 may also be made by a casting method. Furthermore, any number of fillers, fibers, flakes such as mica, metal, ceramic, graphite, etc., can be added to the castable materials to make them more impervious to water vapor.

[0050] While various descriptions of the present invention are described above, it is understood that the various features of the present invention can be used singly or in combination thereof. Therefore, this invention is not to be limited to the specifically preferred embodiments depicted therein.

What is claimed is:

1. A golf ball comprising a cover layer encasing a sub-assembly, the subassembly comprising a barrier layer encasing a core, wherein the barrier layer has a water vapor transmission rate of less than about 0.6 grams·mm/m²·day and a thickness of about 0.001 inches to about 0.1 inches, and comprises a composition comprising at least one curable material and flakes selected from a group consisting of aluminum flakes, iron oxide flakes, micaceous flakes, flaked glass, leafing aluminum flakes, and graphite flakes.

2. The golf ball of claim 1, wherein the composition forms a tortuous path against water vapor encroachment.

3. The golf ball of claim 1, wherein the at least one curable material is selected from a group consisting of:

polymers comprising a recurring unit of RSS, where R is a divalent organic radical, and SS is a disulfide linkage;

polymers comprising a recurring structure of S—CH₂—CH₂—O—CH₂—O—CH₂—CH₂—S; and

polysulfides having an average of at least about 1.8 sulfur atoms per sulfide linkage.

4. The golf ball of claim 1, wherein the curable material is selected from a group consisting of: polythiopolymercaptan polymers; alkyl thiuram polysulfides; solid polysulfides; liquid polysulfides; solvent-dispersed polysulfides; polymers comprising free mercapto groups; hygroscopic polymers; polymers having an elongation-to-break ratio of about 400% to about 500%; reaction products of thio or hydroxyl terminated polysulfides and isocyanate terminated polysulfides or polyisocyanate; and polymers formed from at least one compound selected from the group consisting of aliphatic halide, alkylene chlorides, ethylene dichlorides, oxygen-containing aliphatic halides, bis-beta-chloroethyl ether, bis-beta-chloroethyl formal, and a mixture thereof.

6. The golf ball of claim 1, wherein the composition further comprises one or more substances selected from a group consisting of: deliquescent agents; desiccating agents; accelerating agents; deliquescent accelerating agents; desiccating, deliquescent, dormant curing and accelerating agents; flow-enhancing agents; dormant curing agents; cure-

retarding agents; curing catalysts; chain stoppers; plasticizers; thixotropic agents; antioxidants; heat stabilizers; ionomers; phenolic resins; coumarone-indene resins; polyalkylene polymers; terpene resins; terpene esters; styrene-alkylene copolymers; organic or inorganic reinforcing fibrous materials; element sulfur; sulfur-containing compounds; lower alkyl tin oxides; alkali metal hydroxides; benzothiazyl disulfide; diphenyl guanidine; factice; and mixtures thereof.

7. The golf ball of claim 1, wherein the composition further comprises one or more substances selected from a group consisting of sodium oxide, barium oxide, calcium oxide, manganese dioxide, dibutyl tin oxide, sodium peroxide, barium peroxide, calcium peroxide, zinc peroxide, lead peroxide, sodium pyrophosphate peroxide, sodium carbonate peroxide, sodium perborate, sodium hydroxide, potassium hydroxide, calcium hydroxide, strontium hydroxide, sodium acetate, sodium carbonate, sodium phosphate, sodium molybdate, ammonium dichromate, and dinitro benzene.

8. The golf ball of claim 1, wherein the composition is an anhydrous mixture.

9. The golf ball of claim 1, wherein the composition is substantially cured in less than about 1 hour at about 70° F. to about 75° F.

10. The golf ball of claim 1, wherein the composition effects wetting during formation of the barrier layer.

11. The golf ball of claim 1, wherein the curable material has a viscosity of about 300 centipoises to about 100,000 centipoises and a molecular weight of about 500 to about 500,000.

12. The golf ball of claim 1, wherein the composition is a one-part or two-part formulation that is millable, extrudable, melt-flowable, castable, or injection moldable.

13. The golf ball of claim 1, wherein the subassembly has a Shore D hardness of less than about 60.

14. The golf ball of claim 1, wherein the subassembly has a Shore D hardness of greater than about 50.

15. The golf ball of claim 1, wherein the barrier layer has a specific gravity of greater than about 1.3.

16. A golf ball comprising a cover layer encasing a subassembly, the subassembly comprising a barrier layer encasing a core, wherein the barrier layer has a water vapor transmission rate of less than about 0.6 grams·mm/m²·day and a thickness of about 0.01 inches to about 0.1 inches, and comprises at least one curable material.

17. The golf ball of claim 16, wherein the barrier layer further comprises flakes selected from a group consisting of aluminum flakes, iron oxide flakes, micaceous flakes, flaked glass, leafing aluminum flakes, and graphite flakes.

18. The golf ball of claim 16, wherein the barrier layer has a specific gravity of greater than about 1.2.

19. The golf ball of claim 16, wherein the composition is substantially cured in less than about 1 hour at about 70° F. to about 75° F.

20. A golf ball comprising a cover layer encasing a subassembly, the subassembly comprising a barrier layer encasing a core, wherein the barrier layer has a water vapor transmission rate of less than about 0.6 grams·mm²·day and a thickness of about 0.001 inches to about 0.1 inches, and comprises at least one material selected from a group consisting of: polythiopolymercaptan polymers; alkyl thiuram polysulfides; solid polysulfides; liquid polysulfides; solvent-dispersed polysulfides; polymers comprising free mercapto groups; hygroscopic polymers; polymers having an elongation-to-break ratio of about 400% to about 500%; polymers comprising a recurring structure of S—CH₂—CH₂—O—CH₂—O—CH₂—CH₂—S; polymers comprising a recurring unit of RSS, where R is a divalent organic radical, and SS is a disulfide linkage; polysulfides having an average of at least about 1.8 sulfur atoms per sulfide linkage; reaction products of thio or hydroxyl terminated polysulfides and isocyanate terminated polysulfides or polyisocyanate; and polymers formed from at least one compound selected from the group consisting of aliphatic halide, alkylene chlorides, ethylene dichlorides, oxygen-containing aliphatic halides, bis-beta-chloroethyl ether, bis-beta-chloroethyl formal, and a mixture thereof.

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