



(11) **EP 3 329 971 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
18.11.2020 Bulletin 2020/47

(51) Int Cl.:
A63B 37/00 (2006.01)

(21) Application number: **17192516.7**

(22) Date of filing: **18.04.2013**

(54) **GOLF BALL**

GOLFBALL

BALLE DE GOLF

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **25.04.2012 JP 2012099641**
22.05.2012 JP 2012116542
24.05.2012 JP 2012118422
24.05.2012 JP 2012118544
31.05.2012 JP 2012124249
31.05.2012 JP 2012124924

(43) Date of publication of application:
06.06.2018 Bulletin 2018/23

(62) Document number(s) of the earlier application(s) in accordance with Art. 76 EPC:
13164343.9 / 2 656 882

(73) Proprietor: **Sumitomo Rubber Industries, Ltd.**
Kobe-shi, Hyogo-ken (JP)

(72) Inventors:
• **ISOGAWA, Kazuhiko**
Kobe-shi, Hyogo 651-0072 (JP)
• **TACHIBANA, Kosuke**
Kobe-shi, Hyogo 651-0072 (JP)

(74) Representative: **Manitz Finsterwald**
Patent- und Rechtsanwaltspartnerschaft mbB
Martin-Greif-Strasse 1
80336 München (DE)

(56) References cited:
US-A1- 2008 146 377 US-A1- 2009 227 394
US-A1- 2011 159 998 US-A1- 2012 088 604
US-B2- 7 850 548

EP 3 329 971 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] This application claims priority on Patent Application No. 2012-99641 filed in JAPAN on April 25, 2012, Patent Application No. 2012-116542 filed in JAPAN on May 22, 2012, Patent Application No. 2012-118422 filed in JAPAN on May 24, 2012, Patent Application No. 2012-118544 filed in JAPAN on May 24, 2012, Patent Application No. 2012-124924 filed in JAPAN on May 31, 2012, and Patent Application No. 2012-124249 filed in JAPAN on May 31, 2012.

BACKGROUND OF THE INVENTION

Field of the Invention

[0002] The present invention relates to golf balls. Specifically, the present invention relates to golf balls that include a solid core, a mid layer, and a cover.

Description of the Related Art

[0003] Golf players' foremost requirement for golf balls is flight performance. In particular, golf players place importance on flight performance upon a shot with a driver. Flight performance correlates with the resilience performance of a golf ball. When a golf ball having excellent resilience performance is hit, the golf ball flies at a high speed, thereby achieving a large flight distance. Golf balls that include a core having excellent resilience performance are disclosed in JP61-37178, JP2008-212681 (US2008/0214324), JP2008-523952 (US2006/0135287 and US2007/0173607), and JP2009-119256 (US2009/0124757).

[0004] The core disclosed in JP61-37178 is obtained from a rubber composition that includes a co-crosslinking agent and a crosslinking activator. This publication discloses palmitic acid, stearic acid, and myristic acid as the crosslinking activator.

[0005] The core disclosed in JP2008-212681 is obtained from a rubber composition that includes an organic peroxide, a metal salt of an α,β -unsaturated carboxylic acid, and a copper salt of a fatty acid.

[0006] The core disclosed in JP2008-523952 is obtained from a rubber composition that includes a metal salt of an unsaturated monocarboxylic acid, a free radical initiator, and a non-conjugated diene monomer.

[0007] The core disclosed in JP2009-119256 is obtained from a rubber composition that includes a polybutadiene whose vinyl content is equal to or less than 2%, whose cis 1,4-bond content is equal to or greater than 80%, and which has an active end modified with an alkoxysilane compound.

[0008] An appropriate trajectory height is required in order to achieve a large flight distance. A trajectory height depends on a spin rate and a launch angle. With a golf ball that achieves a high trajectory by a high spin rate, a flight distance is insufficient. With a golf ball that achieves a high trajectory by a high launch angle, a large flight distance is obtained. Use of an outer-hard/inner-soft structure in a golf ball can achieve a low spin rate and a high launch angle. Modifications regarding a hardness distribution of a core are disclosed in JP6-154357 (USP5,403,010), JP2008-194471 (USP7,344,455, US2008/0194358, US2008/0194359, and US2008/0214325), and JP2008-194473 (US2008/0194357 and US2008/0312008).

[0009] In the core disclosed in JP6-154357, a JIS-C hardness H1 at the central point of the core is 58 to 73, a JIS-C hardness H2 in a region that extends over a distance range from equal to or greater than 5 mm to equal to or less than 10 mm from the central point is equal to or greater than 65 but equal to or less than 75, a JIS-C hardness H3 at a point located at a distance of 15 mm from the central point is equal to or greater than 74 but equal to or less than 82, and a JIS-C hardness H4 at the surface of the core is equal to or greater than 76 but equal to or less than 84. The hardness H2 is greater than the hardness H1, the hardness H3 is greater than the hardness H2, and the hardness H4 is equal to or greater than the hardness H3.

[0010] In the core disclosed in JP2008-194471, a Shore D hardness at the central point of the core is equal to or greater than 30 but equal to or less than 48, a Shore D hardness at a point located at a distance of 4 mm from the central point is equal to or greater than 34 but equal to or less than 52, a Shore D hardness at a point located at a distance of 8 mm from the central point is equal to or greater than 40 but equal to or less than 58, a Shore D hardness at a point located at a distance of 12 mm from the central point is equal to or greater than 43 but equal to or less than 61, a Shore D hardness in a region that extends over a distance range from equal to or greater than 2 mm to equal to or less than 3 mm from the surface of the core is equal to or greater than 36 but equal to or less than 54, and a Shore D hardness at the surface is equal to or greater than 41 but equal to or less than 59.

[0011] In the core disclosed in JP2008-194473, a Shore D hardness at the central point of the core is equal to or greater than 25 but equal to or less than 45, a Shore D hardness in a region that extends over a distance range from equal to or greater than 5 mm to equal to or less than 10 mm from the central point is equal to or greater than 39 but equal to or less than 58, a Shore D hardness at a point located at a distance of 15 mm from the central point is equal

to or greater than 36 but equal to or less than 55, and a Shore D hardness at the surface of the core is equal to or greater than 55 but equal to or less than 75.

[0012] JP2010-253268 (US2010/0273575) discloses a golf ball that includes a core, an envelope layer, a mid layer, and a cover. In the core, the hardness gradually increases from the central point of the core to the surface of the core. The difference between a JIS-C hardness at the surface and a JIS-C hardness at the central point is equal to or greater than 15. The hardness of the cover is greater than the hardness of the mid layer, and the hardness of the mid layer is greater than the hardness of the envelope layer.

[0013] Golf players also place importance on controllability of golf balls. Controllability depends on spin rate. When a backspin rate is high, the run is short. It is easy for golf players to cause a golf ball, to which backspin is easily provided, to stop at a target point. When a sidespin rate is high, the golf ball tends to curve. It is easy for golf players to intentionally cause a golf ball, to which sidespin is easily provided, to curve. A golf ball to which spin is easily provided has excellent controllability. In particular, advanced golf players place importance on controllability upon a shot with a short iron.

[0014] Golf players are also interested in durability of golf balls. When being hit with a driver or the like, a golf ball receives great shock and deforms. When a local load is applied to a part of the ball due to the deformation, the golf ball is broken. A golf ball that is resistant to deformation caused by hitting can be continuously used over a long period of time.

[0015] As described above, when a golf ball having a high launch angle and a low spin rate is hit with a driver, a large flight distance is obtained. However, a golf ball having a low spin rate has inferior controllability. Golf players desire achievement of both a desired flight distance and desired controllability. Furthermore, a golf ball that has excellent durability against hitting and can be continuously used is desired. An object of the present invention is to provide a golf ball that has excellent flight performance upon a shot with a driver and excellent controllability upon a shot with a short iron and excellent durability.

US 7 850 548 B2 discloses a multi-piece solid golf ball comprising a core, an envelope layer encasing the core, an intermediate layer encasing the envelope layer and a cover which encases the intermediate layer. The core diameter is disclosed to be between 31 and 38 mm.

Another multi-piece solid golf ball comprising a core, an envelope layer encasing the core, an intermediate layer encasing the envelope layer and a cover which encases the intermediate layer with a core diameter between 31 and 38 mm is disclosed in US 2008/145377 A1.

SUMMARY OF THE INVENTION

[0016] A golf ball according to a first aspect of the present invention (not claimed) includes a spherical core, an inner mid layer positioned outside the core, an outer mid layer positioned outside the inner mid layer, and a cover positioned outside the outer mid layer. When distances (%) from a central point of the core to nine points and JIS-C hardnesses at the nine points, which nine points are obtained by dividing a region from the central point of the core to a surface of the core at intervals of 12.5% of a radius of the core, are plotted in a graph, R^2 of a linear approximation curve obtained by a least-square method is equal to or greater than 0.95. A Shore D hardness H_{m1} of the inner mid layer is greater than a Shore D hardness H_{m2} of the outer mid layer. A Shore D hardness H_c of the cover is less than the hardness H_{m1} . A thickness T_2 of the outer mid layer is equal to or greater than 0.5 mm but equal to or less than 1.6 mm. In the golf ball according to the present invention, a hardness distribution is appropriate. In the golf ball, the energy loss is low when being hit. The golf ball has excellent resilience performance. When the golf ball is hit with a driver, the spin rate is low. The great resilience performance and the low spin rate achieve a large flight distance. When the golf ball is hit with a short iron, the spin rate is high. The golf ball has excellent controllability. In the golf ball, the local load applied when being hit is low. The golf ball has excellent durability. Furthermore, in the golf ball, soft feel at impact is obtained.

[0017] According to another aspect (not claimed), a golf ball according to the present invention includes a spherical core, an inner mid layer positioned outside the core, an outer mid layer positioned outside the inner mid layer, and a cover positioned outside the outer mid layer. When distances (%) from a central point of the core to nine points and JIS-C hardnesses at the nine points, which nine points are obtained by dividing a region from the central point of the core to a surface of the core at intervals of 12.5% of a radius of the core, are plotted in a graph, R^2 of a linear approximation curve obtained by a least-square method is equal to or greater than 0.95. A Shore D hardness H_{m2} of the outer mid layer is greater than a Shore D hardness H_{m1} of the inner mid layer. A Shore D hardness H_c of the cover is less than the hardness H_{m2} . The hardness H_{m1} is less than 50. In the golf ball according to the present invention, a hardness distribution is appropriate. In the golf ball, the energy loss is low when being hit. The golf ball has excellent resilience performance. When the golf ball is hit with a driver, the spin rate is low. The great resilience performance and the low spin rate achieve a large flight distance. When the golf ball is hit with a short iron, the spin rate is high. The golf ball has excellent controllability. In the golf ball, the local load applied when being hit is low. The golf ball has excellent durability.

[0018] According to still another aspect, a golf ball according to the present invention includes a core, a mid layer positioned outside the core, an inner cover positioned outside the mid layer, and an outer cover positioned outside the inner cover. The core has a diameter of equal to or greater than 38.0 mm. When distances (%) from a central point of

the core to nine points and JIS-C hardnesses at the nine points, which nine points are obtained by dividing a region from the central point of the core to a surface of the core at intervals of 12.5% of a radius of the core, are plotted in a graph, R^2 of a linear approximation curve obtained by a least-square method is equal to or greater than 0.95. A Shore D hardness H_m of the mid layer is greater than a Shore D hardness H_{c1} of the inner cover. The hardness H_m is greater than a Shore D hardness H_{c2} of the outer cover. A thickness T_1 of the inner cover is equal to or greater than 0.1 mm but equal to or less than 0.8 mm. In the golf ball according to the present invention, a hardness distribution is appropriate. In the golf ball, the energy loss is low when being hit. When the golf ball is hit with a driver, the spin rate is low. The low spin rate achieves a large flight distance. When the golf ball is hit with a short iron, the spin rate is high. The golf ball has excellent controllability.

[0019] According to still another aspect, a golf ball according to the present invention includes a core, a mid layer positioned outside the core, an inner cover positioned outside the mid layer, and an outer cover positioned outside the inner cover. The core has a diameter of equal to or greater than 38.0 mm. When distances (%) from a central point of the core to nine points and JIS-C hardnesses at the nine points, which nine points are obtained by dividing a region from the central point of the core to a surface of the core at intervals of 12.5% of a radius of the core, are plotted in a graph, R^2 of a linear approximation curve obtained by a least-square method is equal to or greater than 0.95. A Shore D hardness H_m of the mid layer is greater than a Shore D hardness H_{c1} of the inner cover. A Shore D hardness H_{c2} of the outer cover is greater than the hardness H_{c1} . In the golf ball according to the present invention, a hardness distribution is appropriate. In the golf ball, the energy loss is low when being hit. When the golf ball is hit with a driver, the spin rate is low. The low spin rate achieves a large flight distance. When the golf ball is hit with a short iron, the spin rate is high. The golf ball has excellent controllability.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020]

FIG. 1 is a partially cutaway cross-sectional view of a golf ball according to a first embodiment of the present invention; FIG. 2 is a line graph showing a hardness distribution of a core of the golf ball in FIG. 1; FIG. 3 is a partially cutaway cross-sectional view of a golf ball according to a second embodiment of the present invention; FIG. 4 is a line graph showing a hardness distribution of a core of the golf ball in FIG. 3; FIG. 5 is a partially cutaway cross-sectional view of a golf ball according to a third embodiment of the present invention; FIG. 6 is a line graph showing a hardness distribution of a core of the golf ball in FIG. 5; FIG. 7 is a partially cutaway cross-sectional view of a golf ball according to a fourth embodiment of the present invention; and FIG. 8 is a line graph showing a hardness distribution of a core of the golf ball in FIG. 7.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0021] The following will describe in detail the present invention, based on preferred embodiments with reference to the accompanying drawings.

[First Embodiment - not claimed]

[0022] A golf ball 2 shown in FIG. 1 includes a spherical core 4, an inner mid layer 6 positioned outside the core 4, an outer mid layer 8 positioned outside the inner mid layer 6, a reinforcing layer 10 positioned outside the outer mid layer 8, and a cover 12 positioned outside the reinforcing layer 10. On the surface of the cover 12, a large number of dimples 14 are formed. Of the surface of the golf ball 2, a part other than the dimples 14 is a land 16. The golf ball 2 includes a paint layer and a mark layer on the external side of the cover 12, but these layers are not shown in the drawing.

[0023] The golf ball 2 has a diameter of 40 mm or greater but 45 mm or less. From the standpoint of conformity to the rules established by the United States Golf Association (USGA), the diameter is preferably equal to or greater than 42.67 mm. In light of suppression of air resistance, the diameter is preferably equal to or less than 44 mm and more preferably equal to or less than 42.80 mm. The golf ball 2 has a weight of 40 g or greater but 50 g or less. In light of attainment of great inertia, the weight is preferably equal to or greater than 44 g and more preferably equal to or greater than 45.00 g. From the standpoint of conformity to the rules established by the USGA, the weight is preferably equal to or less than 45.93 g.

[0024] The core 4 is obtained by crosslinking a rubber composition. The rubber composition includes:

- (a) a base rubber;

- (b) a co-crosslinking agent;
- (c) a crosslinking initiator; and
- (d) an acid and/or a salt.

5 **[0025]** Examples of the base rubber (a) include polybutadienes, polyisoprenes, styrene-butadiene copolymers, ethylene-propylene-diene copolymers, and natural rubbers. In light of resilience performance, polybutadienes are preferred. When a polybutadiene and another rubber are used in combination, it is preferred that the polybutadiene is included as a principal component. Specifically, the proportion of the polybutadiene to the entire base rubber is preferably equal to or greater than 50% by weight and more preferably equal to or greater than 80% by weight. The proportion of cis-1, 4
10 bonds in the polybutadiene is preferably equal to or greater than 40% by weight and more preferably equal to or greater than 80% by weight.

[0026] A polybutadiene in which the proportion of 1,2-vinyl bonds is equal to or less than 2.0% by weight is preferred. The polybutadiene can contribute to the resilience performance of the core 4. In this respect, the proportion of 1,2-vinyl bonds is preferably equal to or less than 1.7% by weight and particularly preferably equal to or less than 1.5% by weight.

15 **[0027]** From the standpoint that a polybutadiene having a low proportion of 1,2-vinyl bonds and excellent polymerization activity is obtained, a polybutadiene synthesized with a rare-earth-element-containing catalyst is preferred. In particular, a polybutadiene synthesized with a catalyst containing neodymium, which is a lanthanum-series rare earth element compound, is preferred.

20 **[0028]** The polybutadiene has a Mooney viscosity (ML_{1+4} (100°C)) of preferably 30 or greater, more preferably 32 or greater, and particularly preferably 35 or greater. The Mooney viscosity (ML_{1+4} (100°C)) is preferably equal to or less than 140, more preferably equal to or less than 120, even more preferably equal to or less than 100, and particularly preferably equal to or less than 80. The Mooney viscosity (ML_{1+4} (100°C)) is measured according to the standards of "JIS K6300". The measurement conditions are as follows.

25 Rotor: L rotor
Preheating time: 1 minute
Rotating time of rotor: 4 minutes
Temperature: 100°C

30 **[0029]** In light of workability, the polybutadiene has a molecular weight distribution (Mw/Mn) of preferably 2.0 or greater, more preferably 2.2 or greater, even more preferably 2.4 or greater, and particularly preferably 2.6 or greater. In light of resilience performance, the molecular weight distribution (Mw/Mn) is preferably equal to or less than 6.0, more preferably equal to or less than 5.0, even more preferably equal to or less than 4.0, and particularly preferably equal to or less than 3.4. The molecular weight distribution (Mw/Mn) is calculated by dividing the weight average molecular weight Mw by the
35 number average molecular weight Mn.

[0030] The molecular weight distribution is measured by gel permeation chromatography ("HLC-8120GPC" manufactured by Tosoh Corporation). The measurement conditions are as follows.

40 Detector: differential refractometer
Column: GMHXL (manufactured by Tosoh Corporation)
Column temperature: 40°C
Mobile phase: tetrahydrofuran

The molecular weight distribution is calculated as a value obtained by conversion using polystyrene standard.

45 **[0031]** The co-crosslinking agent (b) is:

- (b1) an α , β -unsaturated carboxylic acid having 3 to 8 carbon atoms; and/or
- (b2) a metal salt of an α , β -unsaturated carboxylic acid having 3 to 8 carbon atoms.

50 **[0032]** The rubber composition may include only the α , β -unsaturated carboxylic acid (b1) or only the metal salt (b2) of the α , β -unsaturated carboxylic acid as the co-crosslinking agent (b). The rubber composition may include both the α , β -unsaturated carboxylic acid (b1) and the metal salt (b2) of the α , β -unsaturated carboxylic acid as the co-crosslinking agent (b).

55 **[0033]** The metal salt (b2) of the α , β -unsaturated carboxylic acid graft-polymerizes with the molecular chain of the base rubber, thereby crosslinking the rubber molecules. When the rubber composition includes the α , β -unsaturated carboxylic acid (b1), the rubber composition preferably further includes a metal compound (e). The metal compound (e) reacts with the α , β -unsaturated carboxylic acid (b1) in the rubber composition. A salt obtained by this reaction graft-polymerizes with the molecular chain of the base rubber.

5 [0034] Examples of the metal compound (e) include metal hydroxides such as magnesium hydroxide, zinc hydroxide, calcium hydroxide, sodium hydroxide, lithium hydroxide, potassium hydroxide, and copper hydroxide; metal oxides such as magnesium oxide, calcium oxide, zinc oxide, and copper oxide; and metal carbonates such as magnesium carbonate, zinc carbonate, calcium carbonate, sodium carbonate, lithium carbonate, and potassium carbonate. A compound that includes a bivalent metal is preferred. The compound that includes the bivalent metal reacts with the co-crosslinking agent (b) to form metal crosslinks. The metal compound (e) is particularly preferably a zinc compound. Two or more metal compounds may be used in combination.

10 [0035] Examples of the α , β -unsaturated carboxylic acid (b1) include acrylic acid, methacrylic acid, fumaric acid, maleic acid, and crotonic acid. Examples of the metal component in the metal salt (b2) of the α , β -unsaturated carboxylic acid include sodium ion, potassium ion, lithium ion, magnesium ion, calcium ion, zinc ion, barium ion, cadmium ion, aluminum ion, tin ion, and zirconium ion. The metal salt (b2) of the α , β -unsaturated carboxylic acid may include two or more types of ions. From the standpoint that metal crosslinks are likely to occur between the rubber molecules, bivalent metal ions such as magnesium ion, calcium ion, zinc ion, barium ion, and cadmium ion are preferred. The metal salt (b2) of the α , β -unsaturated carboxylic acid is particularly preferably zinc acrylate.

15 [0036] In light of resilience performance of the golf ball 2, the amount of the co-crosslinking agent (b) is preferably equal to or greater than 15 parts by weight and particularly preferably equal to or greater than 20 parts by weight, per 100 parts by weight of the base rubber. In light of feel at impact, the amount is preferably equal to or less than 50 parts by weight, more preferably equal to or less than 45 parts by weight, and particularly preferably equal to or less than 40 parts by weight, per 100 parts by weight of the base rubber.

20 [0037] The crosslinking initiator (c) is preferably an organic peroxide. The organic peroxide contributes to the resilience performance of the golf ball 2. Examples of preferable organic peroxides include dicumyl peroxide, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, and di-t-butyl peroxide. In light of versatility, dicumyl peroxide is preferred.

25 [0038] In light of resilience performance of the golf ball 2, the amount of the crosslinking initiator (c) is preferably equal to or greater than 0.2 parts by weight and particularly preferably equal to or greater than 0.5 parts by weight, per 100 parts by weight of the base rubber. In light of feel at impact and durability of the golf ball 2, the amount is preferably equal to or less than 5 parts by weight and particularly preferably equal to or less than 2.5 parts by weight, per 100 parts by weight of the base rubber.

30 [0039] The acid component included in the acid and/or the salt (d) has reactivity with a cationic component. During heating and forming of the core 4, the acid dissociates and reacts with the cationic component of the co-crosslinking agent (b). It is thought that the acid inhibits formation of the metal crosslinks by the co-crosslinking agent (b) in the central portion of the core 4. The acid component included in the salt exchanges the cationic component with the co-crosslinking agent (b). It is inferred that during heating and forming of the core 4, the salt breaks the metal crosslinks by the co-crosslinking agent (b) in the central portion of the core 4.

35 [0040] Examples of the acid and/or the salt (d) include oxo acids, such as carboxylic acids, sulfonic acids, and phosphoric acid, and salts thereof; and hydroacids, such as hydrochloric acid and hydrofluoric acid, and salts thereof. Oxo acids and salts thereof are preferred. In light of affinity with the base rubber, the acid and/or the salt (d) is preferably a carboxylic acid and/or a salt thereof (d1). In the present invention, the co-crosslinking agent (b) is not included in the concept of the acid and/or the salt (d).

40 [0041] In light of reactivity with the co-crosslinking agent (b), the carbon number of the carboxylic acid component of the carboxylic acid and/or the salt thereof (d1) is preferably equal to or greater than 1 and more preferably equal to or greater than 5. The carbon number of the carboxylic acid component of the carboxylic acid and/or the salt thereof (d1) is preferably equal to or less than 30 and particularly preferably equal to or less than 20. Examples of preferable carboxylic acids and/or salts thereof (d1) include aliphatic carboxylic acids (fatty acids) and salts thereof, and aromatic carboxylic acids and salts thereof. In light of affinity with the base rubber, fatty acids and salts thereof are preferred.

45 [0042] The rubber composition may include a saturated fatty acid and a salt thereof or may include an unsaturated fatty acid and a salt thereof. The saturated fatty acid and the salt thereof are more preferred.

50 [0043] Examples of fatty acids include butyric acid (C4), valeric acid (C5), caproic acid (C6), enanthic acid (C7), caprylic acid (octanoic acid) (C8), pelargonic acid (C9), capric acid (decanoic acid) (C10), lauric acid (C12), myristic acid (C14), myristoleic acid (C14), pentadecylic acid (C15), palmitic acid (C16), palmitoleic acid (C16), margaric acid (C17), stearic acid (C18), elaidic acid (C18), vaccenic acid (C18), oleic acid (C18), linolic acid (C18), linolenic acid (C18), 12-hydroxystearic acid (C18), arachidic acid (C20), gadoleic acid (C20), arachidonic acid (C20), eicosenoic acid (C20), behenic acid (C22), erucic acid (C22), lignoceric acid (C24), nervonic acid (C24), cerotic acid (C26), montanic acid (C28), and melissic acid (C30). Two or more fatty acids may be used in combination. Caprylic acid (octanoic acid), lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, and behenic acid are preferred.

55 [0044] An aromatic carboxylic acid has an aromatic ring and a carboxyl group. Examples of aromatic carboxylic acids include benzoic acid, phthalic acid, isophthalic acid, terephthalic acid, hemimellitic acid (benzene-1,2,3-tricarboxylic acid), trimellitic acid (benzene-1,2,4-tricarboxylic acid), trimesic acid (benzene-1,3,5-tricarboxylic acid), mellophanic acid

(benzene-1,2,3,4-tetracarboxylic acid), prehnitic acid (benzene-1,2,3,5-tetracarboxylic acid), pyromellitic acid (benzene-1,2,4,5-tetracarboxylic acid), mellitic acid (benzene hexacarboxylic acid), diphenic acid (biphenyl-2,2'-dicarboxylic acid), toluic acid (methylbenzoic acid), xylic acid, prehnitylic acid (2,3,4-trimethylbenzoic acid), γ -isodurylic acid (2,3,5-trimethylbenzoic acid), durylic acid (2,4,5-trimethylbenzoic acid), β -isodurylic acid (2,4,6-trimethylbenzoic acid), α -isodurylic acid (3,4,5-trimethylbenzoic acid), cuminic acid (4-isopropylbenzoic acid), uvitic acid (5-methylisophthalic acid), α -toluic acid (phenylacetic acid), hydratropic acid (2-phenylpropanoic acid), and hydrocinnamic acid (3-phenylpropanoic acid).

[0045] The rubber composition may include an aromatic carboxylic acid substituted with a hydroxyl group, an alkoxy group, or an oxo group. Specific examples of this carboxylic acid can include salicylic acid (2-hydroxybenzoic acid), anisic acid (methoxybenzoic acid), cresotinic acid (hydroxy(methyl) benzoic acid), o-homosalicylic acid (2-hydroxy-3-methylbenzoic acid), m-homosalicylic acid (2-hydroxy-4-methylbenzoic acid), p-homosalicylic acid (2-hydroxy-5-methylbenzoic acid), o-pyrocatechuic acid (2, 3-dihydroxybenzoic acid), β -resorcylic acid (2,4-dihydroxybenzoic acid), γ -resorcylic acid (2,6-dihydroxybenzoic acid), protocatechuic acid (3,4-dihydroxybenzoic acid), α -resorcylic acid (3,5-dihydroxybenzoic acid), vanillic acid (4-hydroxy-3-methoxybenzoic acid), isovanillic acid (3-hydroxy-4-methoxybenzoic acid), veratric acid (3,4-dimethoxybenzoic acid), o-veratric acid (2,3-dimethoxybenzoic acid), orsellinic acid (2,4-dihydroxy-6-methylbenzoic acid), m-hemipinic acid (4,5-dimethoxyphthalic acid), gallic acid (3,4,5-trihydroxybenzoic acid), syringic acid (4-hydroxy-3,5-dimethoxybenzoic acid), asaronic acid (2,4,5-trimethoxybenzoic acid), mandelic acid ((4-hydroxy(phenyl)acetic acid), vanillylmandelic acid (hydroxy(4-hydroxy-3-methoxyphenyl)acetic acid), homoanilic acid ((4-methoxyphenyl)acetic acid), homogentisic acid ((2,5-dihydroxyphenyl)acetic acid), homopyrocatechuic acid ((3,4-dihydroxyphenyl)acetic acid), homovanillic acid ((4-hydroxy-3-methoxyphenyl)acetic acid), homoisovanillic acid ((3-hydroxy-4-methoxyphenyl)acetic acid), homoveratric acid ((3,4-dimethoxyphenyl)acetic acid), o-homoveratric acid ((2,3-dimethoxyphenyl)acetic acid), homophthalic acid (2-(carboxymethyl)benzoic acid), homoisophthalic acid (3-(carboxymethyl)benzoic acid), homoterephthalic acid (4-(carboxymethyl)benzoic acid), phthalonic acid (2-(carboxycarbonyl)benzoic acid), isophthalonic acid (3-(carboxycarbonyl)benzoic acid), terephthalonic acid (4-(carboxycarbonyl)benzoic acid), benzilic acid (hydroxydiphenylacetic acid), atrolactic acid (2-hydroxy-2-phenylpropanoic acid), tropic acid (3-hydroxy-2-phenylpropanoic acid), melilotic acid (3-(2-hydroxyphenyl)propanoic acid), phloretic acid (3-(4-hydroxyphenyl)propanoic acid), hydrocaffeic acid (3-(3,4-dihydroxyphenyl)propanoic acid), hydroferulic acid (3-(4-hydroxy-3-methoxyphenyl)propanoic acid), hydroisoferulic acid (3-(3-hydroxy-4-methoxyphenyl)propanoic acid), p-coumaric acid (3-(4-hydroxyphenyl)acrylic acid), umbellic acid (3-(2,4-dihydroxyphenyl)acrylic acid), caffeic acid (3-(3,4-dihydroxyphenyl)acrylic acid), ferulic acid (3-(4-hydroxy-3-methoxyphenyl)acrylic acid), isoferulic acid (3-(3-hydroxy-4-methoxyphenyl)acrylic acid), and sinapic acid (3-(4-hydroxy-3,5-dimethoxyphenyl)acrylic acid).

[0046] The cationic component included in the acid and/or the salt (d) is a metal ion or an organic cation. Examples of the metal ion include sodium ion, potassium ion, lithium ion, silver ion, magnesium ion, calcium ion, zinc ion, barium ion, cadmium ion, copper ion, cobalt ion, nickel ion, manganese ion, aluminum ion, iron ion, tin ion, zirconium ion, and titanium ion. Two or more types of ions may be used in combination. Zinc ion and magnesium ion are preferred.

[0047] The organic cation is a cation having a carbon chain. Examples of the organic cation include organic ammonium ions. Examples of organic ammonium ions include primary ammonium ions such as stearyl ammonium ion, hexyl ammonium ion, octyl ammonium ion, and 2-ethylhexyl ammonium ion; secondary ammonium ions such as dodecyl(lauryl) ammonium ion, and octadecyl(stearyl) ammonium ion; tertiary ammonium ions such as trioctyl ammonium ion; and quaternary ammonium ions such as dioctyldimethyl ammonium ion, and distearyldimethyl ammonium ion. Two or more types of organic cations may be used in combination.

[0048] In light of ease of the above cation exchange reaction, a salt of a fatty acid is particularly preferred. A fatty acid and a salt of a fatty acid may be used in combination, and salts of two or more fatty acids may be used in combination.

[0049] Examples of preferable salts of carboxylic acids include potassium salts, magnesium salts, aluminum salts, zinc salts, iron salts, copper salts, nickel salts, and cobalt salts of octanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, and behenic acid. Zinc salts of carboxylic acids are particularly preferred. Examples of particularly preferable salts of carboxylic acids include zinc octoate, zinc laurate, zinc myristate, and zinc stearate.

[0050] From the standpoint that a hardness distribution of the core 4 is made appropriate, the amount of the acid and/or the salt (d) is preferably equal to or greater than 0.5 parts by weight, more preferably equal to or greater than 1.0 parts by weight, even more preferably equal to or greater than 1.5 parts by weight, and further preferably equal to or greater than 2 parts by weight, per 100 parts by weight of the base rubber. In light of resilience performance, the amount is preferably equal to or less than 45 parts by weight, more preferably equal to or less than 40 parts by weight, and particularly preferably equal to or less than 30 parts by weight, per 100 parts by weight of the base rubber.

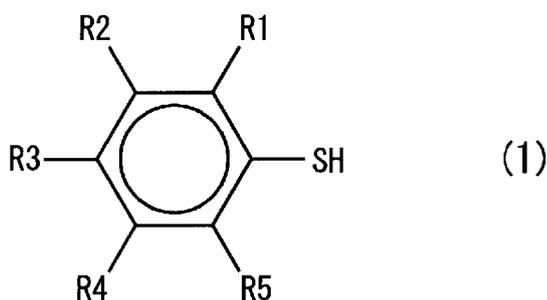
[0051] The weight ratio of the co-crosslinking agent (b) and the acid and/or the salt (d) in the rubber composition is preferably equal to or greater than 3/7 but equal to or less than 9/1, and is particularly preferably equal to or greater than 4/6 but equal to or less than 8/2. From the rubber composition in which this weight ratio is within the above range, the core 4 whose hardness linearly increases from its central point toward its surface is obtained.

[0052] As the co-crosslinking agent (b), zinc acrylate is preferably used. Zinc acrylate whose surface is coated with stearic acid or zinc stearate for the purpose of improving dispersibility to rubber is present. When the rubber composition

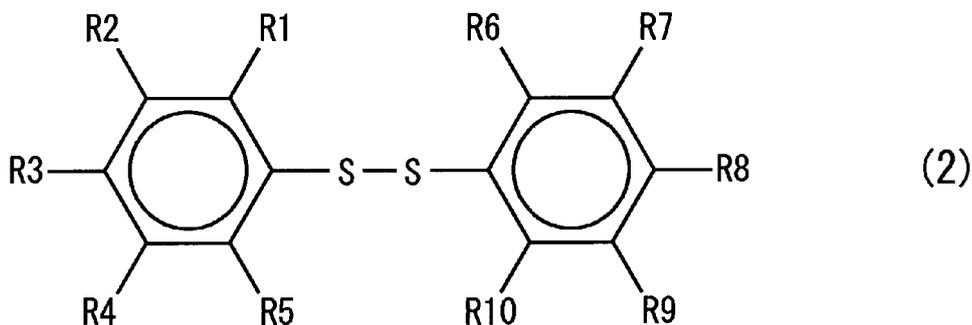
includes this zinc acrylate, the stearic acid or zinc stearate coating the zinc acrylate is not included in the concept of the acid and/or the salt (d).

[0053] The rubber composition preferably further includes an organic sulfur compound (f). The organic sulfur compound (f) can contribute to control of: the linearity of the hardness distribution of the core 4; and the degree of an outer-hard/inner-soft structure. An example of the organic sulfur compound (f) is an organic compound having a thiol group or a polysulfide linkage having 2 to 4 sulfur atoms. A metal salt of this organic compound is also included in the organic sulfur compound (f). Examples of the organic sulfur compound (f) include aliphatic compounds such as aliphatic thiols, aliphatic thiocarboxylic acids, aliphatic dithiocarboxylic acids, and aliphatic polysulfides; heterocyclic compounds; alicyclic compounds such as alicyclic thiols, alicyclic thiocarboxylic acids, alicyclic dithiocarboxylic acids, and alicyclic polysulfides; and aromatic compounds. Specific examples of the organic sulfur compound (f) include thiophenols, thionaphthols, polysulfides, thiocarboxylic acids, dithiocarboxylic acids, sulfenamides, thiurams, dithiocarbamates, and thiazoles. Preferable organic sulfur compounds (e) are thiophenols, diphenyl disulfides, thionaphthols, thiuram disulfides, and metal salts thereof.

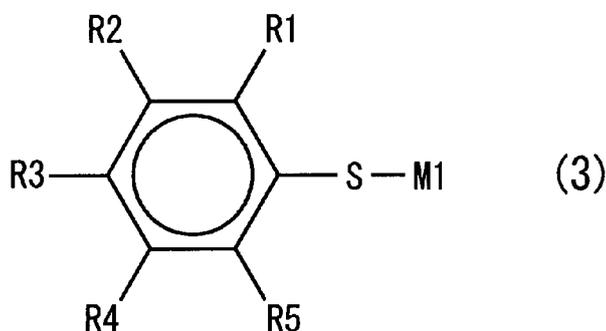
[0054] Specific examples of the organic sulfur compound (f) are represented by the following chemical formulas (1) to (4).



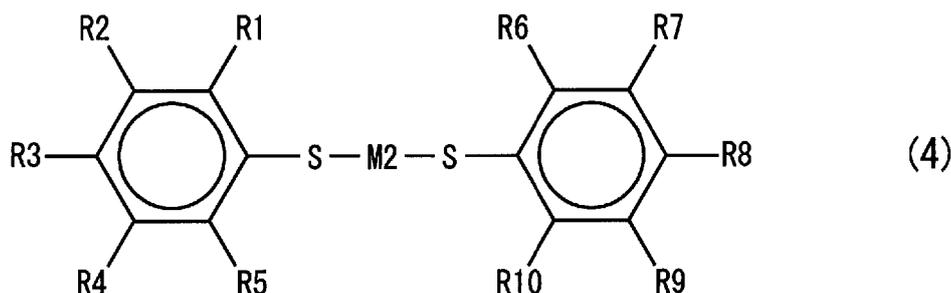
[0055] In the chemical formula (1), R1 to R5 each represent H or a substituent.



[0056] In the chemical formula (2), R1 to R10 each represent H or a substituent.



[0057] In the chemical formula (3), R1 to R5 each represent H or a substituent, and M1 represents a monovalent metal atom.



[0058] In the chemical formula (4), R1 to R10 each represent H or a substituent, and M2 represents a bivalent metal atom.

[0059] In the formulas (1) to (4), each substituent is at least one group selected from the group consisting of a halogen group (F, Cl, Br, I), an alkyl group, a carboxyl group (-COOH), an ester (-COOR) of a carboxyl group, a formyl group (-CHO), an acyl group (-COR), a carbonyl halide group (-COX), a sulfo group (-SO₃H), an ester (-SO₃R) of a sulfo group, a sulfonyl halide group (-SO₂X), a sulfinio group (-SO₂H), an alkylsulfinyl group (-SOR), a carbamoyl group (-CONH₂), an alkyl halide group (-CN), and an alkoxy group (-OR).

[0060] Examples of the organic sulfur compound represented by the chemical formula (1) include thiophenols substituted with halogen groups, such as 4-fluorothiophenol, 2,5-difluorothiophenol, 2,4,5-trifluorothiophenol, 2,4,5,6-tetrafluorothiophenol, pentafluorothiophenol, 2-chlorothiophenol, 4-chlorothiophenol, 2,4-dichlorothiophenol, 2,5-dichlorothiophenol, 2,6-dichlorothiophenol, 2,4,5-trichlorothiophenol, 2,4,5,6-tetrachlorothiophenol, pentachlorothiophenol, 4-bromothiophenol, 2,5-dibromothiophenol, 2,4,5-tribromothiophenol, 2,4,5,6-tetrabromothiophenol, pentabromothiophenol, 4-iodothiophenol, 2,5-diiodothiophenol, 2,4,5-triiodothiophenol, 2,4,5,6-tetraiodothiophenol, and penta-iodothiophenol; thiophenols substituted with alkyl groups, such as 4-methylthiophenol, 2,4,5-trimethylthiophenol, pentamethylthiophenol, 4-t-butylthiophenol, 2,4,5-tri-t-butylthiophenol, and penta-t-butylthiophenol; thiophenols substituted with carboxyl groups, such as 4-carboxythiophenol, 2,4,6-tricarboxythiophenol, and pentacarboxythiophenol; thiophenols substituted with alkoxy carbonyl groups, such as 4-methoxycarbonylthiophenol, 2,4,6-trimethoxycarbonylthiophenol, and pentamethoxycarbonylthiophenol; thiophenols substituted with formyl groups, such as 4-formylthiophenol, 2,4,6-triformylthiophenol, and pentaformylthiophenol; thiophenols substituted with acyl groups, such as 4-acetylthiophenol, 2,4,6-triacetylthiophenol, and pentaacetylthiophenol; thiophenols substituted with carbonyl halide groups, such as 4-chlorocarbonylthiophenol, 2,4,6-tri(chlorocarbonyl)thiophenol, and penta(chlorocarbonyl)thiophenol; thiophenols substituted with sulfo groups, such as 4-sulfothiophenol, 2,4,6-trisulfothiophenol, and pentasulfothiophenol; thiophenols substituted with alkoxy sulfonyl groups, such as 4-methoxysulfonylthiophenol, 2,4,6-trimethoxysulfonylthiophenol, and pentamethoxysulfonylthiophenol; thiophenols substituted with sulfonyl halide groups, such as 4-chlorosulfonylthiophenol, 2,4,6-tri(chlorosulfonyl)thiophenol, and penta(chlorosulfonyl)thiophenol; thiophenols substituted with sulfinio groups, such as 4-sulfiniothiophenol, 2,4,6-trisulfiniothiophenol, and pentasulfiniothiophenol; thiophenols substituted with alkylsulfinyl groups, such as 4-methylsulfinylthiophenol, 2,4,6-tri(methylsulfinyl)thiophenol, and penta(methylsulfinyl)thiophenol; thiophenols substituted with carbamoyl groups, such as 4-carbamoylthiophenol, 2,4,6-tricarbamoylthiophenol, and pentacarbamoylthiophenol; thiophenols substituted with alkyl halide groups, such as 4-trichloromethylthiophenol, 2,4,6-tri(trichloromethyl)thiophenol, and penta(trichloromethyl)thiophenol; thiophenols substituted with cyano groups, such as 4-cyanothiophenol, 2,4,6-tricyanothiophenol, and pentacyanothiophenol; and thiophenols substituted with alkoxy groups, such as 4-methoxythiophenol, 2,4,6-trimethoxythiophenol, and pentamethoxythiophenol. Each of these thiophenols is substituted with one type of substituent.

[0061] Another example of the organic sulfur compound represented by the chemical formula (1) is a compound substituted with at least one type of the above substituents and another substituent. Examples of the other substituent include a nitro group (-NO₂), an amino group (-NH₂), a hydroxyl group (-OH), and a phenylthio group (-SPh). Specific examples of the compound include 4-chloro-2-nitrothiophenol, 4-chloro-2-aminothiophenol, 4-chloro-2-hydroxythiophenol, 4-chloro-2-phenylthiothiophenol, 4-methyl-2-nitrothiophenol, 4-methyl-2-aminothiophenol, 4-methyl-2-hydroxythiophenol, 4-methyl-2-phenylthiothiophenol, 4-carboxy-2-nitrothiophenol, 4-carboxy-2-aminothiophenol, 4-carboxy-2-hydroxythiophenol, 4-carboxy-2-phenylthiothiophenol, 4-methoxycarbonyl-2-nitrothiophenol, 4-methoxycarbonyl-2-aminothiophenol, 4-methoxycarbonyl-2-hydroxythiophenol, 4-methoxycarbonyl-2-phenylthiothiophenol, 4-formyl-2-nitrothiophenol, 4-formyl-2-aminothiophenol, 4-formyl-2-hydroxythiophenol, 4-formyl-2-phenylthiothiophenol, 4-acetyl-2-nitrothiophenol, 4-acetyl-2-aminothiophenol, 4-acetyl-2-hydroxythiophenol, 4-acetyl-2-phenylthiothiophenol, 4-chlorocarbonyl-2-nitrothiophenol, 4-chlorocarbonyl-2-aminothiophenol, 4-chlorocarbonyl-2-hydroxythiophenol, 4-chlorocarbonyl-2-phenylthiothiophenol, 4-sulfo-2-nitrothiophenol, 4-sulfo-2-aminothiophenol, 4-sulfo-2-hydroxythiophenol, 4-sulfo-2-phenylthiothiophenol, 4-methoxysulfonyl-2-nitrothiophenol, 4-methoxysulfonyl-2-aminothiophenol, 4-methoxysulfonyl-2-hydroxythiophenol, 4-methoxysulfonyl-2-phenylthiothiophenol, 4-chlorosulfonyl-2-nitrothiophenol, 4-chlorosulfonyl-2-

aminothiophenol, 4-chlorosulfonyl-2-hydroxythiophenol, 4-chlorosulfonyl-2-phenylthiophenol, 4-sulfinyl-2-nitrothiophenol, 4-sulfinyl-2-aminothiophenol, 4-sulfinyl-2-hydroxythiophenol, 4-sulfinyl-2-phenylthiophenol, 4-methylsulfinyl-2-nitrothiophenol, 4-methylsulfinyl-2-aminothiophenol, 4-methylsulfinyl-2-hydroxythiophenol, 4-methylsulfinyl-2-phenylthiophenol, 4-carbamoyl-2-nitrothiophenol, 4-carbamoyl-2-aminothiophenol, 4-carbamoyl-2-hydroxythiophenol, 4-carbamoyl-2-phenylthiophenol, 4-trichloromethyl-2-nitrothiophenol, 4-trichloromethyl-2-aminothiophenol, 4-trichloromethyl-2-hydroxythiophenol, 4-trichloromethyl-2-phenylthiophenol, 4-cyano-2-nitrothiophenol, 4-cyano-2-aminothiophenol, 4-cyano-2-hydroxythiophenol, 4-cyano-2-phenylthiophenol, 4-methoxy-2-nitrothiophenol, 4-methoxy-2-aminothiophenol, 4-methoxy-2-hydroxythiophenol, and 4-methoxy-2-phenylthiophenol.

[0062] Still another example of the organic sulfur compound represented by the chemical formula (1) is a compound substituted with two or more types of substituents. Specific examples of the compound include 4-acetyl-2-chlorothiophenol, 4-acetyl-2-methylthiophenol, 4-acetyl-2-carboxythiophenol, 4-acetyl-2-methoxycarbonylthiophenol, 4-acetyl-2-formylthiophenol, 4-acetyl-2-chlorocarbonylthiophenol, 4-acetyl-2-sulfothiophenol, 4-acetyl-2-methoxysulfonylthiophenol, 4-acetyl-2-chlorosulfonylthiophenol, 4-acetyl-2-sulfinylthiophenol, 4-acetyl-2-methylsulfinylthiophenol, 4-acetyl-2-carbamoylthiophenol, 4-acetyl-2-trichloromethylthiophenol, 4-acetyl-2-cyanothiophenol, and 4-acetyl-2-methoxythiophenol.

[0063] Examples of the organic sulfur compound represented by the chemical formula (2) include diphenyl disulfide; diphenyl disulfides substituted with halogen groups, such as bis(4-fluorophenyl)disulfide, bis(2,5-difluorophenyl)disulfide, bis(2,4,5-trifluorophenyl)disulfide, bis(2,4,5,6-tetrafluorophenyl)disulfide, bis(pentafluorophenyl)disulfide, bis(4-chlorophenyl)disulfide, bis(2,5-dichlorophenyl)disulfide, bis(2,4,5-trichlorophenyl)disulfide, bis(2,4,5,6-tetrachlorophenyl)disulfide, bis(pentachlorophenyl)disulfide, bis(4-bromophenyl)disulfide, bis(2,5-dibromophenyl)disulfide, bis(2,4,5-tribromophenyl)disulfide, bis(2,4,5,6-tetrabromophenyl)disulfide, bis(pentabromophenyl)disulfide, bis(4-iodophenyl)disulfide, bis(2,5-diiodophenyl)disulfide, bis(2,4,5-triiodophenyl)disulfide, bis(2,4,5,6-tetraiodophenyl)disulfide, and bis(pentaiodophenyl)disulfide; diphenyl disulfides substituted with alkyl groups, such as bis(4-methylphenyl)disulfide, bis(2,4,5-trimethylphenyl)disulfide, bis(pentamethylphenyl)disulfide, bis(4-t-butylphenyl)disulfide, bis(2,4,5-tri-t-butylphenyl)disulfide, and bis(penta-t-butylphenyl)disulfide; diphenyl disulfides substituted with carboxyl groups, such as bis(4-carboxyphenyl)disulfide, bis(2,4,6-tricarboxyphenyl)disulfide, and bis(pentacarboxyphenyl)disulfide; diphenyl disulfides substituted with alkoxy carbonyl groups, such as bis(4-methoxycarbonylphenyl)disulfide, bis(2,4,6-trimethoxycarbonylphenyl)disulfide, and bis(pentamethoxycarbonylphenyl)disulfide; diphenyl disulfides substituted with formyl groups, such as bis(4-formylphenyl)disulfide, bis(2,4,6-triformylphenyl)disulfide, and bis(pentaformylphenyl)disulfide; diphenyl disulfides substituted with acyl groups, such as bis(4-acetylphenyl)disulfide, bis(2,4,6-triacetylphenyl)disulfide, and bis(pentaacetylphenyl)disulfide; diphenyl disulfides substituted with carbonyl halide groups, such as bis(4-chlorocarbonylphenyl)disulfide, bis(2,4,6-tri(chlorocarbonyl)phenyl)disulfide, and bis(penta(chlorocarbonyl)phenyl)disulfide; diphenyl disulfides substituted with sulfo groups, such as bis(4-sulfophenyl)disulfide, bis(2,4,6-trisulfophenyl)disulfide, and bis(pentasulfophenyl)disulfide; diphenyl disulfides substituted with alkoxy sulfonyl groups, such as bis(4-methoxysulfonylphenyl)disulfide, bis(2,4,6-trimethoxysulfonylphenyl)disulfide, and bis(pentamethoxysulfonylphenyl)disulfide; diphenyl disulfides substituted with sulfonyl halide groups, such as bis(4-chlorosulfonylphenyl)disulfide, bis(2,4,6-tri(chlorosulfonyl)phenyl)disulfide, and bis(penta(chlorosulfonyl)phenyl)disulfide; diphenyl disulfides substituted with sulfinyl groups, such as bis(4-sulfinophenyl)disulfide, bis(2,4,6-trisulfinophenyl)disulfide, and bis(pentasulfinophenyl)disulfide; diphenyl disulfides substituted with alkylsulfinyl groups, such as bis(4-methylsulfinylphenyl)disulfide, bis(2,4,6-tri(methylsulfinyl)phenyl)disulfide, and bis(penta(methylsulfinyl)phenyl)disulfide; diphenyl disulfides substituted with carbamoyl groups, such as bis(4-carbamoylphenyl)disulfide, bis(2,4,6-tricarbamoylphenyl)disulfide, and bis(pentacarbamoylphenyl)disulfide; diphenyl disulfides substituted with alkyl halide groups, such as bis(4-trichloromethylphenyl)disulfide, bis(2,4,6-tri(trichloromethyl)phenyl)disulfide, and bis(penta(trichloromethyl)phenyl)disulfide; diphenyl disulfides substituted with cyano groups, such as bis(4-cyanophenyl)disulfide, bis(2,4,6-tricyanophenyl)disulfide, and bis(pentacyanophenyl)disulfide; and diphenyl disulfides substituted with alkoxy groups, such as bis(4-methoxyphenyl)disulfide, bis(2,4,6-trimethoxyphenyl)disulfide, and bis(pentamethoxyphenyl)disulfide. Each of these diphenyl disulfides is substituted with one type of substituent.

[0064] Another example of the organic sulfur compound represented by the chemical formula (2) is a compound substituted with at least one type of the above substituents and another substituent. Examples of the other substituent include a nitro group (-NO₂), an amino group (-NH₂), a hydroxyl group (-OH), and a phenylthio group (-SPh). Specific examples of the compound include bis(4-chloro-2-nitrophenyl)disulfide, bis(4-chloro-2-aminophenyl)disulfide, bis(4-chloro-2-hydroxyphenyl)disulfide, bis(4-chloro-2-phenylthiophenyl)disulfide, bis(4-methyl-2-nitrophenyl)disulfide, bis(4-methyl-2-aminophenyl)disulfide, bis(4-methyl-2-hydroxyphenyl)disulfide, bis(4-methyl-2-phenylthiophenyl)disulfide, bis(4-carboxy-2-nitrophenyl)disulfide, bis(4-carboxy-2-aminophenyl)disulfide, bis(4-carboxy-2-hydroxyphenyl)disulfide, bis(4-carboxy-2-phenylthiophenyl)disulfide, bis(4-methoxycarbonyl-2-nitrophenyl)disulfide, bis(4-methoxycarbonyl-2-aminophenyl)disulfide, bis(4-methoxycarbonyl-2-hydroxyphenyl)disulfide, bis(4-methoxycarbonyl-2-phenylthiophenyl)disulfide, bis(4-formyl-2-nitrophenyl)disulfide, bis(4-formyl-2-aminophenyl)disulfide, bis(4-formyl-2-hydroxyphenyl)disulfide, bis(4-formyl-2-phenylthiophenyl)disulfide, bis(4-acetyl-2-nitrophenyl)disulfide, bis(4-acetyl-2-aminophenyl)di-

sulfide, bis(4-acetyl-2-hydroxyphenyl)disulfide, bis(4-acetyl-2-phenylthiophenyl)disulfide, bis(4-chlorocarbonyl-2-nitrophenyl)disulfide, bis(4-chlorocarbonyl-2-aminophenyl)disulfide, bis(4-chlorocarbonyl-2-hydroxyphenyl)disulfide, bis(4-chlorocarbonyl-2-phenylthiophenyl)disulfide, bis(4-sulfo-2-nitrophenyl)disulfide, bis(4-sulfo-2-aminophenyl)disulfide, bis(4-sulfo-2-hydroxyphenyl)disulfide, bis(4-sulfo-2-phenylthiophenyl)disulfide, bis(4-methoxysulfonyl-2-nitrophenyl)disulfide, bis(4-methoxysulfonyl-2-aminophenyl)disulfide, bis(4-methoxysulfonyl-2-hydroxyphenyl)disulfide, bis(4-methoxysulfonyl-2-phenylthiophenyl)disulfide, bis(4-chlorosulfonyl-2-nitrophenyl)disulfide, bis(4-chlorosulfonyl-2-aminophenyl)disulfide, bis(4-chlorosulfonyl-2-hydroxyphenyl)disulfide, bis(4-chlorosulfonyl-2-phenylthiophenyl)disulfide, bis(4-sulfinyl-2-nitrophenyl)disulfide, bis(4-sulfinyl-2-aminophenyl)disulfide, bis(4-sulfinyl-2-hydroxyphenyl)disulfide, bis(4-sulfinyl-2-phenylthiophenyl)disulfide, bis(4-methylsulfinyl-2-nitrophenyl)disulfide, bis(4-methylsulfinyl-2-aminophenyl)disulfide, bis(4-methylsulfinyl-2-hydroxyphenyl)disulfide, bis(4-methylsulfinyl-2-phenylthiophenyl)disulfide, bis(4-carbamoyl-2-nitrophenyl)disulfide, bis(4-carbamoyl-2-aminophenyl)disulfide, bis(4-carbamoyl-2-hydroxyphenyl)disulfide, bis(4-carbamoyl-2-phenylthiophenyl)disulfide, bis(4-trichloromethyl-2-nitrophenyl)disulfide, bis(4-trichloromethyl-2-aminophenyl)disulfide, bis(4-trichloromethyl-2-hydroxyphenyl)disulfide, bis(4-trichloromethyl-2-phenylthiophenyl)disulfide, bis(4-cyano-2-nitrophenyl)disulfide, bis(4-cyano-2-aminophenyl)disulfide, bis(4-cyano-2-hydroxyphenyl)disulfide, bis(4-cyano-2-phenylthiophenyl)disulfide, bis(4-methoxy-2-nitrophenyl)disulfide, bis(4-methoxy-2-aminophenyl)disulfide, bis(4-methoxy-2-hydroxyphenyl)disulfide, and bis(4-methoxy-2-phenylthiophenyl)disulfide.

[0065] Still another example of the organic sulfur compound represented by the chemical formula (2) is a compound substituted with two or more types of substituents. Specific examples of the compound include bis(4-acetyl-2-chlorophenyl)disulfide, bis(4-acetyl-2-methylphenyl)disulfide, bis(4-acetyl-2-carboxyphenyl)disulfide, bis(4-acetyl-2-methoxycarbonylphenyl)disulfide, bis(4-acetyl-2-formylphenyl)disulfide, bis(4-acetyl-2-chlorocarbonylphenyl)disulfide, bis(4-acetyl-2-sulfo-2-nitrophenyl)disulfide, bis(4-acetyl-2-methoxysulfonylphenyl)disulfide, bis(4-acetyl-2-chlorosulfonylphenyl)disulfide, bis(4-acetyl-2-sulfinylphenyl)disulfide, bis(4-acetyl-2-methylsulfinylphenyl)disulfide, bis(4-acetyl-2-carbamoylphenyl)disulfide, bis(4-acetyl-2-trichloromethylphenyl)disulfide, bis(4-acetyl-2-cyanophenyl)disulfide, and bis(4-acetyl-2-methoxyphenyl)disulfide.

[0066] Examples of the organic sulfur compound represented by the chemical formula (3) include thiophenol sodium salt; thiophenol sodium salts substituted with halogen groups, such as 4-fluorothiophenol sodium salt, 2,5-difluorothiophenol sodium salt, 2,4,5-trifluorothiophenol sodium salt, 2,4,5,6-tetrafluorothiophenol sodium salt, pentafluorothiophenol sodium salt, 4-chlorothiophenol sodium salt, 2,5-dichlorothiophenol sodium salt, 2,4,5-trichlorothiophenol sodium salt, 2,4,5,6-tetrachlorothiophenol sodium salt, pentachlorothiophenol sodium salt, 4-bromothiophenol sodium salt, 2,5-dibromothiophenol sodium salt, 2,4,5-tribromothiophenol sodium salt, 2,4,5,6-tetrabromothiophenol sodium salt, pentabromothiophenol sodium salt, 4-iodothiophenol sodium salt, 2,5-diiodothiophenol sodium salt, 2,4,5-triiodothiophenol sodium salt, 2,4,5,6-tetraiodothiophenol sodium salt, and pentaiodothiophenol sodium salt; thiophenol sodium salts substituted with alkyl groups, such as 4-methylthiophenol sodium salt, 2,4,5-trimethylthiophenol sodium salt, pentamethylthiophenol sodium salt, 4-t-butylthiophenol sodium salt, 2,4,5-tri-t-butylthiophenol sodium salt, and penta (t-butyl) thiophenol sodium salt; thiophenol sodium salts substituted with carboxyl groups, such as 4-carboxythiophenol sodium salt, 2,4,6-tricarboxythiophenol sodium salt, and pentacarboxythiophenol sodium salt; thiophenol sodium salts substituted with alkoxy carbonyl groups, such as 4-methoxycarbonylthiophenol sodium salt, 2,4,6-trimethoxycarbonylthiophenol sodium salt, and pentamethoxycarbonylthiophenol sodium salt; thiophenol sodium salts substituted with formyl groups, such as 4-formylthiophenol sodium salt, 2,4,6-triformylthiophenol sodium salt, and pentaformylthiophenol sodium salt; thiophenol sodium salts substituted with acyl groups, such as 4-acetylthiophenol sodium salt, 2,4,6-triacetylthiophenol sodium salt, and pentaacetylthiophenol sodium salt; thiophenol sodium salts substituted with carbonyl halide groups, such as 4-chlorocarbonylthiophenol sodium salt, 2,4,6-tri(chlorocarbonyl)thiophenol sodium salt, and penta(chlorocarbonyl)thiophenolsodium salt; thiophenolsodium salts substituted with sulfo groups, such as 4-sulfothiophenol sodium salt, 2,4,6-trisulfothiophenol sodium salt, and pentasulfothiophenol sodium salt; thiophenol sodium salts substituted with alkoxy sulfonyl groups, such as 4-methoxysulfonylthiophenol sodium salt, 2,4,6-trimethoxysulfonylthiophenol sodium salt, and pentamethoxysulfonylthiophenol sodium salt; thiophenol sodium salts substituted with sulfonyl halide groups, such as 4-chlorosulfonylthiophenol sodium salt, 2,4,6-tri(chlorosulfonyl)thiophenol sodium salt, and penta(chlorosulfonyl)thiophenolsodium salt; thiophenolsodium salts substituted with sulfinyl groups, such as 4-sulfinylthiophenol sodium salt, 2,4,6-trisulfinylthiophenol sodium salt, and pentasulfinylthiophenol sodium salt; thiophenol sodium salts substituted with alkylsulfinyl groups, such as 4-methylsulfinylthiophenol sodium salt, 2,4,6-tri(methylsulfinyl)thiophenol sodium salt, and penta(methylsulfinyl)thiophenolsodium salt; thiophenolsodium salts substituted with carbamoyl groups, such as 4-carbamoylthiophenol sodium salt, 2,4,6-tricarbamoylthiophenol sodium salt, and pentacarbamoylthiophenol sodium salt; thiophenol sodium salts substituted with alkyl halide groups, such as 4-trichloromethylthiophenol sodium salt, 2,4,6-tri(trichloromethyl)thiophenol sodium salt, and penta(trichloromethyl)thiophenol sodium salt; thiophenol sodium salts substituted with cyano groups, such as 4-cyanothiophenolsodium salt, 2,4,6-tricyanothiophenolsodium salt, and penta-cyanothiophenol sodium salt; and thiophenol sodium salts substituted with alkoxy groups, such as 4-methoxythiophenol sodium salt, 2,4,6-trimethoxythiophenol sodium salt, and pentamethoxythiophenol sodium salt. Each of these thiophenol sodium salts is substituted with one type of substituent.

[0067] Another example of the organic sulfur compound represented by the chemical formula (3) is a compound substituted with at least one type of the above substituents and another substituent. Examples of the other substituent include a nitro group (-NO₂), an amino group (-NH₂), a hydroxyl group (-OH), and a phenylthio group (-SPh). Specific examples of the compound include 4-chloro-2-nitrothiophenol sodium salt, 4-chloro-2-aminothiophenol sodium salt, 4-chloro-2-hydroxythiophenol sodium salt, 4-chloro-2-phenylthiothiophenol sodium salt, 4-methyl-2-nitrothiophenol sodium salt, 4-methyl-2-aminothiophenol sodium salt, 4-methyl-2-hydroxythiophenol sodium salt, 4-methyl-2-phenylthiothiophenol sodium salt, 4-carboxy-2-nitrothiophenol sodium salt, 4-carboxy-2-aminothiophenol sodium salt, 4-carboxy-2-hydroxythiophenol sodium salt, 4-carboxy-2-phenylthiothiophenol sodium salt, 4-methoxycarbonyl-2-nitrothiophenol sodium salt, 4-methoxycarbonyl-2-aminothiophenol sodium salt, 4-methoxycarbonyl-2-hydroxythiophenol sodium salt, 4-methoxycarbonyl-2-phenylthiothiophenol sodium salt, 4-formyl-2-nitrothiophenol sodium salt, 4-formyl-2-aminothiophenol sodium salt, 4-formyl-2-hydroxythiophenol sodium salt, 4-formyl-2-phenylthiothiophenol sodium salt, 4-acetyl-2-nitrothiophenol sodium salt, 4-acetyl-2-aminothiophenol sodium salt, 4-acetyl-2-hydroxythiophenol sodium salt, 4-acetyl-2-phenylthiothiophenol sodium salt, 4-chlorocarbonyl-2-nitrothiophenol sodium salt, 4-chlorocarbonyl-2-aminothiophenol sodium salt, 4-chlorocarbonyl-2-hydroxythiophenol sodium salt, 4-chlorocarbonyl-2-phenylthiothiophenol sodium salt, 4-sulfo-2-nitrothiophenol sodium salt, 4-sulfo-2-aminothiophenol sodium salt, 4-sulfo-2-hydroxythiophenol sodium salt, 4-sulfo-2-phenylthiothiophenol sodium salt, 4-methoxysulfonyl-2-nitrothiophenol sodium salt, 4-methoxysulfonyl-2-aminothiophenol sodium salt, 4-methoxysulfonyl-2-hydroxythiophenol sodium salt, 4-methoxysulfonyl-2-phenylthiothiophenol sodium salt, 4-chlorosulfonyl-2-nitrothiophenol sodium salt, 4-chlorosulfonyl-2-aminothiophenol sodium salt, 4-chlorosulfonyl-2-hydroxythiophenol sodium salt, 4-chlorosulfonyl-2-phenylthiothiophenol sodium salt, 4-sulfino-2-nitrothiophenol sodium salt, 4-sulfino-2-aminothiophenol sodium salt, 4-sulfino-2-hydroxythiophenol sodium salt, 4-sulfino-2-phenylthiothiophenol sodium salt, 4-methylsulfinyl-2-nitrothiophenol sodium salt, 4-methylsulfinyl-2-aminothiophenol sodium salt, 4-methylsulfinyl-2-hydroxythiophenol sodium salt, 4-methylsulfinyl-2-phenylthiothiophenol sodium salt, 4-carbamoyl-2-nitrothiophenol sodium salt, 4-carbamoyl-2-aminothiophenol sodium salt, 4-carbamoyl-2-hydroxythiophenol sodium salt, 4-carbamoyl-2-phenylthiothiophenol sodium salt, 4-trichloromethyl-2-nitrothiophenol sodium salt, 4-trichloromethyl-2-aminothiophenol sodium salt, 4-trichloromethyl-2-hydroxythiophenol sodium salt, 4-trichloromethyl-2-phenylthiothiophenol sodium salt, 4-cyano-2-nitrothiophenol sodium salt, 4-cyano-2-aminothiophenol sodium salt, 4-cyano-2-hydroxythiophenol sodium salt, 4-cyano-2-phenylthiothiophenol sodium salt, 4-methoxy-2-nitrothiophenol sodium salt, 4-methoxy-2-aminothiophenol sodium salt, 4-methoxy-2-hydroxythiophenol sodium salt, and 4-methoxy-2-phenylthiothiophenol sodium salt.

[0068] Still another example of the organic sulfur compound represented by the chemical formula (3) is a compound substituted with two or more types of substituents. Specific examples of the compound include 4-acetyl-2-chlorothiophenol sodium salt, 4-acetyl-2-methylthiophenol sodium salt, 4-acetyl-2-carboxythiophenol sodium salt, 4-acetyl-2-methoxycarbonylthiophenol sodium salt, 4-acetyl-2-formylthiophenol sodium salt, 4-acetyl-2-chlorocarbonylthiophenol sodium salt, 4-acetyl-2-sulfothiophenol sodium salt, 4-acetyl-2-methoxysulfonylthiophenol sodium salt, 4-acetyl-2-chlorosulfonylthiophenol sodium salt, 4-acetyl-2-sulfinothiophenol sodium salt, 4-acetyl-2-methylsulfinylthiophenol sodium salt, 4-acetyl-2-carbamoylthiophenol sodium salt, 4-acetyl-2-trichloromethylthiophenol sodium salt, 4-acetyl-2-cyanothiophenol sodium salt, and 4-acetyl-2-methoxythiophenol sodium salt. Examples of the monovalent metal represented by M1 in the chemical formula (3) include sodium, lithium, potassium, copper (I), and silver (I).

[0069] Examples of the organic sulfur compound represented by the chemical formula (4) include thiophenol zinc salt; thiophenol zinc salts substituted with halogen groups, such as 4-fluorothiophenol zinc salt, 2,5-difluorothiophenol zinc salt, 2,4,5-trifluorothiophenol zinc salt, 2,4,5,6-tetrafluorothiophenol zinc salt, pentafluorothiophenol zinc salt, 4-chlorothiophenol zinc salt, 2,5-dichlorothiophenol zinc salt, 2,4,5-trichlorothiophenol zinc salt, 2,4,5,6-tetrachlorothiophenol zinc salt, pentachlorothiophenol zinc salt, 4-bromothiophenol zinc salt, 2,5-dibromothiophenol zinc salt, 2,4,5-tribromothiophenol zinc salt, 2,4,5,6-tetrabromothiophenol zinc salt, pentabromothiophenol zinc salt, 4-iodothiophenol zinc salt, 2,5-diiodothiophenol zinc salt, 2,4,5-triiodothiophenol zinc salt, 2,4,5,6-tetraiodothiophenol zinc salt, and pentaiodothiophenol zinc salt; thiophenol zinc salts substituted with alkyl groups, such as 4-methylthiophenol zinc salt, 2,4,5-trimethylthiophenol zinc salt, pentamethylthiophenol zinc salt, 4-t-butylthiophenol zinc salt, 2,4,5-tri-t-butylthiophenol zinc salt, and penta-t-butylthiophenol zinc salt; thiophenol zinc salts substituted with carboxyl groups, such as 4-carboxythiophenol zinc salt, 2,4,6-tricarboxythiophenol zinc salt, and pentacarboxythiophenol zinc salt; thiophenol zinc salts substituted with alkoxy carbonyl groups, such as 4-methoxycarbonylthiophenol zinc salt, 2,4,6-trimethoxycarbonylthiophenol zinc salt, and pentamethoxycarbonylthiophenol zinc salt; thiophenol zinc salts substituted with formyl groups, such as 4-formylthiophenol zinc salt, 2,4,6-triformylthiophenol zinc salt, and pentaformylthiophenol zinc salt; thiophenol zinc salts substituted with acyl groups, such as 4-acetylthiophenol zinc salt, 2,4,6-triacetylthiophenol zinc salt, and pentaacetylthiophenol zinc salt; thiophenol zinc salts substituted with carbonyl halide groups, such as 4-chlorocarbonylthiophenol zinc salt, 2,4,6-tri(chlorocarbonyl)thiophenol zinc salt, and penta(chlorocarbonyl)thiophenol zinc salt; thiophenol zinc salts substituted with sulfo groups, such as 4-sulfothiophenol zinc salt, 2,4,6-trisulfothiophenol zinc salt, and pentasulfothiophenol zinc salt; thiophenol zinc salts substituted with alkoxy sulfonyl groups, such as 4-methoxysulfonylthiophenol zinc salt, 2,4,6-trimethoxysulfonylthiophenol zinc salt, and pentamethoxysulfonylthiophenol zinc salt; thiophenol zinc

salts substituted with sulfonyl halide groups, such as 4-chlorosulfonylthiophenol zinc salt, 2,4,6-tri(chlorosulfonyl)thiophenol zinc salt, and penta(chlorosulfonyl)thiophenol zinc salt; thiophenol zinc salts substituted with sulfinio groups, such as 4-sulfiniothiophenol zinc salt, 2,4,6-trisulfiniothiophenol zinc salt, and pentasulfiniothiophenol zinc salt; thiophenol zinc salts substituted with alkylsulfinyl groups, such as 4-methylsulfinylthiophenol zinc salt, 2,4,6-tri(methylsulfinyl)thiophenol zinc salt, and penta(methylsulfinyl)thiophenol zinc salt; thiophenol zinc salts substituted with carbamoyl groups, such as 4-carbamoylthiophenol zinc salt, 2,4,6-tricarbamoylthiophenol zinc salt, and pentacarbamoylthiophenol zinc salt; thiophenol zinc salts substituted with alkyl halide groups, such as 4-trichloromethylthiophenol zinc salt, 2,4,6-tri(trichloromethyl)thiophenol zinc salt, and penta(trichloromethyl)thiophenol zinc salt; thiophenol zinc salts substituted with cyano groups, such as 4-cyanothiophenol zinc salt, 2,4,6-tricyanothiophenol zinc salt, and pentacyanothiophenol zinc salt; and thiophenol zinc salts substituted with alkoxy groups, such as 4-methoxythiophenol zinc salt, 2,4,6-trimethoxythiophenol zinc salt, and pentamethoxythiophenol zinc salt. Each of these thiophenol zinc salts is substituted with one type of substituent.

[0070] Another example of the organic sulfur compound represented by the chemical formula (4) is a compound substituted with at least one type of the above substituents and another substituent. Examples of the other substituent include a nitro group (-NO₂), an amino group (-NH₂), a hydroxyl group (-OH), and a phenylthio group (-SPh). Specific examples of the compound include 4-chloro-2-nitrothiophenol zinc salt, 4-chloro-2-aminothiophenol zinc salt, 4-chloro-2-hydroxythiophenol zinc salt, 4-chloro-2-phenylthiothiophenol zinc salt, 4-methyl-2-nitrothiophenol zinc salt, 4-methyl-2-aminothiophenol zinc salt, 4-methyl-2-hydroxythiophenol zinc salt, 4-methyl-2-phenylthiothiophenol zinc salt, 4-carboxy-2-nitrothiophenol zinc salt, 4-carboxy-2-aminothiophenol zinc salt, 4-carboxy-2-hydroxythiophenol zinc salt, 4-carboxy-2-phenylthiothiophenol zinc salt, 4-methoxycarbonyl-2-nitrothiophenol zinc salt, 4-methoxycarbonyl-2-aminothiophenol zinc salt, 4-methoxycarbonyl-2-hydroxythiophenol zinc salt, 4-methoxycarbonyl-2-phenylthiothiophenol zinc salt, 4-formyl-2-nitrothiophenol zinc salt, 4-formyl-2-aminothiophenol zinc salt, 4-formyl-2-hydroxythiophenol zinc salt, 4-formyl-2-phenylthiothiophenol zinc salt, 4-acetyl-2-nitrothiophenol zinc salt, 4-acetyl-2-aminothiophenol zinc salt, 4-acetyl-2-hydroxythiophenol zinc salt, 4-acetyl-2-phenylthiothiophenol zinc salt, 4-chlorocarbonyl-2-nitrothiophenol zinc salt, 4-chlorocarbonyl-2-aminothiophenol zinc salt, 4-chlorocarbonyl-2-hydroxythiophenol zinc salt, 4-chlorocarbonyl-2-phenylthiothiophenol zinc salt, 4-sulfo-2-nitrothiophenol zinc salt, 4-sulfo-2-aminothiophenol zinc salt, 4-sulfo-2-hydroxythiophenol zinc salt, 4-sulfo-2-phenylthiothiophenol zinc salt, 4-methoxysulfonyl-2-nitrothiophenol zinc salt, 4-methoxysulfonyl-2-aminothiophenol zinc salt, 4-methoxysulfonyl-2-hydroxythiophenol zinc salt, 4-methoxysulfonyl-2-phenylthiothiophenol zinc salt, 4-chlorosulfonyl-2-nitrothiophenol zinc salt, 4-chlorosulfonyl-2-aminothiophenol zinc salt, 4-chlorosulfonyl-2-hydroxythiophenol zinc salt, 4-chlorosulfonyl-2-phenylthiothiophenol zinc salt, 4-sulfinio-2-nitrothiophenol zinc salt, 4-sulfinio-2-aminothiophenol zinc salt, 4-sulfinio-2-hydroxythiophenol zinc salt, 4-sulfinio-2-phenylthiothiophenol zinc salt, 4-methylsulfinyl-2-nitrothiophenol zinc salt, 4-methylsulfinyl-2-aminothiophenol zinc salt, 4-methylsulfinyl-2-hydroxythiophenol zinc salt, 4-methylsulfinyl-2-phenylthiothiophenol zinc salt, 4-carbamoyl-2-nitrothiophenol zinc salt, 4-carbamoyl-2-aminothiophenol zinc salt, 4-carbamoyl-2-hydroxythiophenol zinc salt, 4-carbamoyl-2-phenylthiothiophenol zinc salt, 4-trichloromethyl-2-nitrothiophenol zinc salt, 4-trichloromethyl-2-aminothiophenol zinc salt, 4-trichloromethyl-2-hydroxythiophenol zinc salt, 4-trichloromethyl-2-phenylthiothiophenol zinc salt, 4-cyano-2-nitrothiophenol zinc salt, 4-cyano-2-aminothiophenol zinc salt, 4-cyano-2-hydroxythiophenol zinc salt, 4-cyano-2-phenylthiothiophenol zinc salt, 4-methoxy-2-nitrothiophenol zinc salt, 4-methoxy-2-aminothiophenol zinc salt, 4-methoxy-2-hydroxythiophenol zinc salt, and 4-methoxy-2-phenylthiothiophenol zinc salt.

[0071] Still another example of the organic sulfur compound represented by the chemical formula (4) is a compound substituted with two or more types of substituents. Specific examples of the compound include 4-acetyl-2-chlorothiophenol zinc salt, 4-acetyl-2-methylthiophenol zinc salt, 4-acetyl-2-carboxythiophenol zinc salt, 4-acetyl-2-methoxycarbonylthiophenol zinc salt, 4-acetyl-2-formylthiophenol zinc salt, 4-acetyl-2-chlorocarbonylthiophenol zinc salt, 4-acetyl-2-sulfothiophenol zinc salt, 4-acetyl-2-methoxysulfonylthiophenol zinc salt, 4-acetyl-2-chlorosulfonylthiophenol zinc salt, 4-acetyl-2-sulfiniothiophenol zinc salt, 4-acetyl-2-methylsulfinylthiophenol zinc salt, 4-acetyl-2-carbamoylthiophenol zinc salt, 4-acetyl-2-trichloromethylthiophenol zinc salt, 4-acetyl-2-cyanothiophenol zinc salt, and 4-acetyl-2-methoxythiophenol zinc salt. Examples of the bivalent metal represented by M2 in the chemical formula (4) include zinc, magnesium, calcium, strontium, barium, titanium (II), manganese (II), iron (II), cobalt (II), nickel (II), zirconium (II), and tin (II).

[0072] Examples of thionaphthols include 2-thionaphthol, 1-thionaphthol, 2-chloro-1-thionaphthol, 2-bromo-1-thionaphthol, 2-fluoro-1-thionaphthol, 2-cyano-1-thionaphthol, 2-acetyl-1-thionaphthol, 1-chloro-2-thionaphthol, 1-bromo-2-thionaphthol, 1-fluoro-2-thionaphthol, 1-cyano-2-thionaphthol, 1-acetyl-2-thionaphthol, and metal salts thereof. 1-thionaphthol, 2-thionaphthol, and zinc salts thereof are preferred.

[0073] Examples of sulfenamide type organic sulfur compounds include N-cyclohexyl-2-benzothiazole sulfenamide, N-oxydiethylene-2-benzothiazole sulfenamide, and N-t-butyl-2-benzothiazole sulfenamide. Examples of thiuram type organic sulfur compounds include tetramethylthiuram monosulfide, tetramethylthiuram disulfide, tetraethylthiuram disulfide, tetrabutylthiuram disulfide, and dipentamethylenethiuram tetrasulfide. Examples of dithiocarbamates include zinc dimethyldithiocarbamate, zinc diethyldithiocarbamate, zinc dibutyldithiocarbamate, zinc ethylphenyldithiocarbamate, sodium dimethyldithiocarbamate, sodium diethyldithiocarbamate, copper (II) dimethyldithiocarbamate, iron (III)

dimethyldithiocarbamate, selenium diethyldithiocarbamate, and tellurium diethyldithiocarbamate. Examples of thiazole type organic sulfur compounds include 2-mercaptobenzothiazole (MBT); dibenzothiazyl disulfide (MBTS); a sodium salt, a zinc salt, a copper salt, and a cyclohexylamine salt of 2-mercaptobenzothiazole; 2-(2,4-dinitrophenyl)mercaptobenzothiazole; and 2-(2,6-diethyl-4-morpholiniothio)benzothiazole.

[0074] Particularly preferable organic sulfur compounds (e) from the standpoint that an outer-hard/inner-soft structure is easily obtained are 2-thionaphthol, bis(pentabromophenyl)disulfide, and 2,6-dichlorothiophenol.

[0075] In light of an outer-hard/inner-soft structure of the core 4, the amount of the organic sulfur compound (f) is preferably equal to or greater than 0.05 parts by weight, more preferably equal to or greater than 0.1 parts by weight, and particularly preferably equal to or greater than 0.2 parts by weight, per 100 parts by weight of the base rubber. In light of resilience performance, the amount is preferably equal to or less than 5 parts by weight, more preferably equal to or less than 3 parts by weight, and particularly preferably equal to or less than 1 parts by weight, per 100 parts by weight of the base rubber.

[0076] For the purpose of adjusting specific gravity and the like, a filler may be included in the core 4. Examples of suitable fillers include zinc oxide, barium sulfate, calcium carbonate, and magnesium carbonate. The amount of the filler is determined as appropriate so that the intended specific gravity of the core 4 is accomplished. A particularly preferable filler is zinc oxide. Zinc oxide serves not only as a specific gravity adjuster but also as a crosslinking activator.

[0077] According to need, an anti-aging agent, a coloring agent, a plasticizer, a dispersant, sulfur, a vulcanization accelerator, and the like are added to the rubber composition of the core 4. Crosslinked rubber powder or synthetic resin powder may also be dispersed in the rubber composition.

[0078] During heating and forming of the core 4, the heat of the crosslinking reaction of the base rubber remains near the central point of the core 4. Thus, during heating and forming of the core 4, the temperature at the central portion is high. The temperature gradually decreases from the central point toward the surface. The acid and/or the salt (d) reacts with a metal salt of the co-crosslinking agent (b) to break metal crosslinks. This reaction is accelerated in a region where the temperature is high. In other words, breaking of the metal crosslinks is likely to occur in the central portion of the core 4 where the temperature is high, and is unlikely to occur near the surface of the core 4. As a result, the crosslinking density of the core 4 increases from its central point toward its surface. In the core 4, the hardness linearly increases from its central point toward its surface. Furthermore, since the rubber composition includes the organic sulfur compound (f) together with the acid and/or the salt (d), the gradient of the hardness distribution can be controlled, and the degree of the outer-hard/inner-soft structure of the core 4 can be increased.

[0079] FIG. 2 is a line graph showing a hardness distribution of the core 4 of the golf ball 2 in FIG. 1 according to the present invention. The horizontal axis of the graph indicates the ratio (%) of a distance from the central point of the core 4 to the radius of the core 4. The vertical axis of the graph indicates a JIS-C hardness. Nine measuring points obtained by dividing a region from the central point of the core 4 to the surface of the core 4 at intervals of 12.5% of the radius of the core 4 are plotted in the graph. The ratio of the distance from the central point of the core 4 to each of these measuring points to the radius of the core 4 is as follows.

First point: 0.0% (central point)

Second point: 12.5%

Third point: 25.0%

Fourth point: 37.5%

Fifth point: 50.0%

Sixth point: 62.5%

Seventh point: 75.0%

Eighth point: 87.5%

Ninth point: 100.0% (surface)

[0080] Hardnesses at the first to eighth points are measured by pressing a JIS-C type hardness scale against a cut plane of the core 4 that has been cut into two halves. A hardness at the ninth point is measured by pressing the JIS-C type hardness scale against the surface of the spherical core 4. For the measurement, an automated rubber hardness measurement machine (trade name "P1", manufactured by Kobunshi Keiki Co., Ltd.), to which this hardness scale is mounted, is used.

[0081] FIG. 2 also shows a linear approximation curve obtained by a least-square method on the basis of the distances and the hardnesses of the nine measuring points. In FIG. 2, the broken line does not greatly deviate from the linear approximation curve. In other words, the broken line has a shape close to the linear approximation curve. That is, in the core 4 according to the present invention, the hardness linearly increases from its central point toward its surface. When the golf ball 2 that includes the core 4 is hit with a driver, the energy loss is low. The core 4 has excellent resilience performance. When the golf ball 2 is hit with a driver, the flight distance is large. In the core 4, the hardness continuously increases from its central point toward its surface. In the core 4, there is no discontinuous point caused by a multilayer

structure. When the golf ball 2 that includes the core 4 deforms by being hit, no local load is applied thereto. The golf ball 2 has excellent durability.

[0082] In the core 4, R^2 of the linear approximation curve obtained by the least-square method is equal to or greater than 0.95. R^2 is an index indicating the linearity of the broken line. For the core 4 for which R^2 is equal to or greater than 0.95, the shape of the broken line of the hardness distribution is close to a straight line. The core 4 for which R^2 is equal to or greater than 0.95 has excellent resilience performance. In this respect, R^2 is more preferably equal to or greater than 0.97 and particularly preferably equal to or greater than 0.99. R^2 is calculated by squaring a correlation coefficient R. The correlation coefficient R is calculated by dividing the covariance of the distance (%) from the central point and the hardness (JIS-C) by the standard deviation of the distance (%) from the central point and the standard deviation of the hardness (JIS-C).

[0083] In the present invention, a JIS-C hardness at a measuring point whose ratio of the distance from the central point of the core 4 to the radius of the core 4 is x% is represented by $H(x)$. The hardness at the central point of the core 4 is represented by $H(0.0)$. The surface hardness of the core 4 is represented by H_s . The difference ($H_s - H(0.0)$) between the surface hardness H_s and the central hardness $H(0.0)$ is equal to or greater than 15. The difference is great. In other words, the core 4 has an outer-hard/inner-soft structure. When the core 4 is hit with a driver, the recoil (torsional return) is great, and thus spin is suppressed. The core 4 contributes to the flight performance of the golf ball 2. In light of flight performance, the difference ($H_s - H(0.0)$) is more preferably equal to or greater than 25 and particularly preferably equal to or greater than 30. From the standpoint that the core 4 can easily be formed, the difference ($H_s - H(0.0)$) is preferably equal to or less than 50.

[0084] The hardness $H(0.0)$ at the central point of the core 4 is preferably equal to or greater than 40 but equal to or less than 70. The golf ball 2 that includes the core 4 having a hardness $H(0.0)$ of 40 or greater has excellent resilience performance. The hardness $H(0.0)$ is more preferably equal to or greater than 45 and particularly preferably equal to or greater than 50. In the core 4 having a hardness $H(0.0)$ of 70 or less, an outer-hard/inner-soft structure can be achieved. In the golf ball 2 that includes the core 4, spin can be suppressed. The hardness $H(0.0)$ is more preferably equal to or less than 68 and particularly preferably equal to or less than 65.

[0085] The hardness H_s at the surface of the core 4 is preferably equal to or greater than 78 but equal to or less than 96. In the core 4 having a hardness H_s of 78 or greater, an outer-hard/inner-soft structure can be achieved. In the golf ball 2 that includes the core 4, spin can be suppressed. The hardness H_s is more preferably equal to or greater than 80 and particularly preferably equal to or greater than 82. The golf ball 2 that includes the core 4 having a hardness H_s of 96 or less has excellent durability. The hardness H_s is more preferably equal to or less than 94 and particularly preferably equal to or less than 92.

[0086] The core 4 preferably has a diameter of 36.0 mm or greater. The core 4 having a diameter of 36.0 mm or greater can achieve excellent resilience performance of the golf ball 2. The core 4 having a diameter of 36.0 mm or greater can achieve an outer-hard/inner-soft structure of the golf ball 2. In this respect, the diameter is more preferably equal to or greater than 37.0 mm and particularly preferably equal to or greater than 38.0 mm. Furthermore, the diameter of the core 4 is preferably equal to or less than 40.1 mm. In the golf ball 2 that includes the core 4 having a diameter of 40.1 mm or less, the inner mid layer 6, the outer mid layer 8, and the cover 12 can have sufficient thicknesses. The golf ball 2 that includes the inner mid layer 6, the outer mid layer 8, and the cover 12 which have large thicknesses has excellent durability. In this respect, the diameter is particularly preferably equal to or less than 38.8 mm.

[0087] In light of feel at impact, the core 4 has an amount of compressive deformation D_c of preferably 3.0 mm or greater and particularly preferably 3.2 mm or greater. In light of resilience performance, the amount of compressive deformation D_c is preferably equal to or less than 3.8 mm and particularly preferably equal to or less than 3.5 mm.

[0088] For the inner mid layer 6, a resin composition is suitably used. Examples of the base resin of the resin composition include ionomer resins, polystyrenes, polyesters, polyamides, and polyolefins.

[0089] Particularly preferable base resins are ionomer resins. The golf ball 2 that includes the inner mid layer 6 including an ionomer resin has excellent resilience performance. An ionomer resin and another resin may be used in combination for the inner mid layer 6. In this case, the principal component of the base resin is preferably the ionomer resin. Specifically, the proportion of the ionomer resin to the entire base resin is preferably equal to or greater than 80% by weight and more preferably equal to or greater than 90% by weight.

[0090] Examples of preferable ionomer resins include binary copolymers formed with an α -olefin and an α , β -unsaturated carboxylic acid having 3 to 8 carbon atoms. A preferable binary copolymer includes 80% by weight or greater but 90% by weight or less of an α -olefin, and 10% by weight or greater but 20% by weight or less of an α , β -unsaturated carboxylic acid. The binary copolymer has excellent resilience performance. Examples of other preferable ionomer resins include ternary copolymers formed with: an α -olefin; an α , β -unsaturated carboxylic acid having 3 to 8 carbon atoms; and an α , β -unsaturated carboxylate ester having 2 to 22 carbon atoms. A preferable ternary copolymer includes 70% by weight or greater but 85% by weight or less of an α -olefin, 5% by weight or greater but 30% by weight or less of an α , β -unsaturated carboxylic acid, and 1% by weight or greater but 25% by weight or less of an α , β -unsaturated carboxylate ester. The ternary copolymer has excellent resilience performance. For the binary copolymers and the ternary copolymers,

preferable α -olefins are ethylene and propylene, while preferable α , β -unsaturated carboxylic acids are acrylic acid and methacrylic acid. A particularly preferable ionomer resin is a copolymer formed with ethylene and acrylic acid or methacrylic acid.

[0091] In the binary copolymers and the ternary copolymers, some of the carboxyl groups are neutralized with metal ions. Examples of metal ions for use in neutralization include sodium ion, potassium ion, lithium ion, zinc ion, calcium ion, magnesium ion, aluminum ion, and neodymium ion. The neutralization may be carried out with two or more types of metal ions. Particularly suitable metal ions in light of resilience performance and durability of the golf ball 2 are sodium ion, zinc ion, lithium ion, and magnesium ion.

[0092] Specific examples of ionomer resins include trade names "Himilan 1555", "Himilan 1557", "Himilan 1605", "Himilan 1706", "Himilan 1707", "Himilan 1856", "Himilan 1855", "Himilan AM7311", "Himilan AM7315", "Himilan AM7317", "Himilan AM7318", "Himilan AM7329", "Himilan MK7320", and "Himilan MK7329", manufactured by Du Pont-MITSUI POLYCHEMICALS Co., Ltd.; trade names "Surlyn 6120", "Surlyn 6910", "Surlyn 7930", "Surlyn 7940", "Surlyn 8140", "Surlyn 8150", "Surlyn 8940", "Surlyn 8945", "Surlyn 9120", "Surlyn 9150", "Surlyn 9910", "Surlyn 9945", "Surlyn AD8546", "HPF1000", and "HPF2000", manufactured by E.I. du Pont de Nemours and Company; and trade names "IOTEK 7010", "IOTEK 7030", "IOTEK 7510", "IOTEK 7520", "IOTEK 8000", and "IOTEK 8030", manufactured by ExxonMobil Chemical Company.

[0093] Two or more ionomer resins may be used in combination for the inner mid layer 6. An ionomer resin neutralized with a monovalent metal ion, and an ionomer resin neutralized with a bivalent metal ion may be used in combination.

[0094] In the inner mid layer 6, a highly elastic resin may be included. Specific examples of the highly elastic resin include polyamides.

[0095] According to need, a coloring agent such as titanium dioxide, a filler such as barium sulfate, a dispersant, an antioxidant, an ultraviolet absorber, a light stabilizer, a fluorescent material, a fluorescent brightener, and the like are included in the resin composition of the inner mid layer 6 in an adequate amount.

[0096] From the standpoint that an outer-hard/inner-soft structure can be achieved in the sphere consisting of the core 4 and the inner mid layer 6, the inner mid layer 6 has a Shore D hardness Hm1 of preferably 55 or greater and more preferably 60 or greater. In the golf ball 2 that includes the inner mid layer 6 having a hardness Hm1 in this range, a spin rate is sufficiently suppressed upon a shot with a driver. The flight distance of the golf ball 2 is large. In light of controllability of the golf ball 2, the hardness Hm1 is preferably equal to or less than 70 and particularly preferably equal to or less than 68. When the golf ball 2 is hit with a short iron, the spin rate is high.

[0097] The Shore D hardness Hm1 of the inner mid layer 6 is measured according to the standards of "ASTM-D 2240-68" with a Shore D type hardness scale mounted to an automated rubber hardness measurement machine (trade name "P1", manufactured by Kobunshi Keiki Co., Ltd.). For the measurement, a slab that is formed by hot press and that has a thickness of about 2 mm is used. A slab kept at 23°C for two weeks is used for the measurement. At the measurement, three slabs are stacked. A slab formed from the same resin composition as the resin composition of the inner mid layer 6 is used.

[0098] The inner mid layer 6 preferably has a thickness T1 of 0.5 mm or greater but 1.6 mm or less. In light of durability, the thickness T1 is more preferably equal to or greater than 0.7 mm. In light of resilience performance, the thickness T1 is more preferably equal to or less than 1.2 mm.

[0099] For the outer mid layer 8, a resin composition is suitably used. Examples of the base resin of the resin composition include ionomer resins, polystyrenes, polyesters, polyamides, and polyolefins.

[0100] Particularly preferable base resins are ionomer resins. The ionomer resins described above for the inner mid layer 6 can also be used for the outer mid layer 8. The golf ball 2 that includes the outer mid layer 8 including an ionomer resin has excellent resilience performance. An ionomer resin and another resin may be used in combination for the outer mid layer 8. In this case, the principal component of the base resin is preferably the ionomer resin. Specifically, the proportion of the ionomer resin to the entire base resin is preferably equal to or greater than 45% by weight and more preferably equal to or greater than 60% by weight.

[0101] A preferable resin that can be used in combination with an ionomer resin is a styrene block-containing thermoplastic elastomer. The styrene block-containing thermoplastic elastomer has excellent compatibility with ionomer resins. A resin composition including the styrene block-containing thermoplastic elastomer has excellent fluidity.

[0102] The styrene block-containing thermoplastic elastomer includes a polystyrene block as a hard segment, and a soft segment. A typical soft segment is a diene block. Examples of compounds for the diene block include butadiene, isoprene, 1,3-pentadiene, and 2,3-dimethyl-1,3-butadiene. Butadiene and isoprene are preferred. Two or more compounds may be used in combination.

[0103] Examples of styrene block-containing thermoplastic elastomers include styrene-butadiene-styrene block copolymers (SBS), styrene-isoprene-styrene block copolymers (SIS), styrene-isoprene-butadiene-styrene block copolymers (SIBS), hydrogenated SBS, hydrogenated SIS, and hydrogenated SIBS. Examples of hydrogenated SBS include styrene-ethylene-butylene-styrene block copolymers (SEBS). Examples of hydrogenated SIS include styrene-ethylene-propylene-styrene block copolymers (SEPS). Examples of hydrogenated SIBS include styrene-ethylene-ethylene-pro-

pylene-styrene block copolymers (SEEPS).

[0104] In light of resilience performance of the golf ball 2, the content of the styrene component in the styrene block-containing thermoplastic elastomer is preferably equal to or greater than 10% by weight, more preferably equal to or greater than 12% by weight, and particularly preferably equal to or greater than 15% by weight. In light of feel at impact of the golf ball 2, the content is preferably equal to or less than 70% by weight, more preferably equal to or less than 65% by weight, and particularly preferably equal to or less than 60% by weight.

[0105] In the present invention, styrene block-containing thermoplastic elastomers include a polymer alloy of an olefin and one or more members selected from the group consisting of SBS, SIS, SIBS, and a hydrogenated product thereof. The olefin component in the polymer alloy is presumed to contribute to improvement of compatibility with ionomer resins. Use of this polymer alloy improves the resilience performance of the golf ball 2. An olefin having 2 to 10 carbon atoms is preferably used. Examples of suitable olefins include ethylene, propylene, butene, and pentene. Ethylene and propylene are particularly preferred.

[0106] Specific examples of polymer alloys include trade names "RabalonT3221C", "RabalonT3339C", "RabalonSJ4400N", "Rabalon SJ5400N", "Rabalon SJ6400N", "Rabalon SJ7400N", "Rabalon SJ8400N", "Rabalon SJ9400N", and "Rabalon SR04", manufactured by Mitsubishi Chemical Corporation. Other specific examples of styrene block-containing thermoplastic elastomers include trade name "Epofriend A1010" manufactured by Daicel Chemical Industries, Ltd., and trade name "Septon HG-252" manufactured by Kuraray Co., Ltd.

[0107] According to need, a coloring agent such as titanium dioxide, a filler such as barium sulfate, a dispersant, an antioxidant, an ultraviolet absorber, a light stabilizer, a fluorescent material, a fluorescent brightener, and the like are included in the resin composition of the outer mid layer 8 in an adequate amount.

[0108] In light of a spin suppression effect upon a shot with a driver, the outer mid layer 8 has a Shore D hardness Hm2 of preferably 25 or greater and more preferably 30 or greater. The flight distance of the golf ball 2 is large. In light of controllability of the golf ball 2, the hardness Hm2 is preferably equal to or less than 60 and particularly preferably equal to or less than 54. When the golf ball 2 is hit with a short iron, the spin rate is high. The hardness Hm2 is measured by the same measurement method as that for the hardness Hm1.

[0109] In light of durability and feel at impact, the hardness Hm1 of the inner mid layer 6 is preferably greater than the hardness Hm2 of the outer mid layer 8. When the golf ball 2 in which the hardness Hm1 is greater than the hardness Hm2 is hit with a driver, the shock provided to the golf ball 2 by the driver is alleviated. The golf ball 2 has excellent durability. The golf ball 2 has soft feel at impact.

[0110] The difference (Hm1-Hm2) between the hardness Hm1 of the inner mid layer 6 and the hardness Hm2 of the outer mid layer 8 is preferably equal to or greater than 8 and particularly preferably equal to or greater than 14. In light of resilience performance, the difference (Hm1-Hm2) is preferably equal to or less than 35. When the golf ball 2 that includes the outer mid layer 8 having a hardness Hm2 in this range is hit with a driver, the spin rate is low. The flight distance of the golf ball 2 is large. When the golf ball 2 is hit with a short iron, the spin rate is high.

[0111] The outer mid layer 8 preferably has a thickness T2 of 0.5 mm or greater. In the golf ball 2 that includes the outer mid layer 8 having a thickness T2 of 0.5 mm or greater, the shock by a hit is alleviated. Thus, the golf ball 2 has excellent durability. In this respect, the thickness T2 is more preferably equal to or greater than 0.7 mm. The thickness T2 is preferably equal to or less than 1.6 mm. The golf ball 2 that includes the outer mid layer 8 having a thickness T2 of 1.6 mm or less includes a relatively large core 4. The golf ball 2 exerts sufficient resilience performance. In this respect, the thickness T2 is particularly preferably equal to or less than 1.2 mm.

[0112] The sum (T1+T2) of the thickness T1 and the thickness T2 is preferably equal to or greater than 1.0 mm. In the golf ball 2, the shock by a hit is alleviated. Thus, the golf ball 2 has excellent durability. In this respect, the sum (T1+T2) is more preferably equal to or greater than 1.3 mm. The sum (T1+T2) is preferably equal to or less than 3.0 mm. The golf ball 2 includes a relatively large core 4. The golf ball 2 exerts sufficient resilience performance. In this respect, the sum (T1+T2) is more preferably equal to or less than 2.0 mm.

[0113] For forming the outer mid layer 8, known methods such as injection molding, compression molding, and the like can be used.

[0114] For the cover 12, a resin composition is suitably used. A preferable base resin of the resin composition is a urethane resin or a urea resin. The principal component of the urethane resin is a polyurethane. The polyurethane is flexible. When the golf ball 2 that includes the cover 12 formed from the resin composition that includes the polyurethane is hit with a short iron, the spin rate is high. The cover 12 formed from this resin composition contributes to controllability upon a shot with a short iron. The polyurethane also contributes to the scuff resistance of the cover 12. Furthermore, the polyurethane can also contribute to excellent feel at impact when the golf ball 2 is hit with a putter or a short iron.

[0115] In light of ease of forming the cover 12, a preferable base resin is a thermoplastic polyurethane elastomer. The thermoplastic polyurethane elastomer includes a polyurethane component as a hard segment, and a polyester component or a polyether component as a soft segment. Examples of isocyanates for the polyurethane component include alicyclic diisocyanates, aromatic diisocyanates, and aliphatic diisocyanates. Two or more diisocyanates may be used in combination.

[0116] Examples of alicyclic diisocyanates include 4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI), 1,3-bis(isocyanatomethyl)cyclohexane (H_6 XDI), isophorone diisocyanate (IPDI), and trans-1,4-cyclohexane diisocyanate (CHDI). In light of versatility and processability, H_{12} MDI is preferred.

[0117] Examples of aromatic diisocyanates include 4,4'-diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI). Examples of aliphatic diisocyanates include hexamethylene diisocyanate (HDI).

[0118] Particularly, alicyclic diisocyanates are preferred. Since an alicyclic diisocyanate does not have any double bond in the main chain, the alicyclic diisocyanate suppresses yellowing of the cover 12. In addition, since an alicyclic diisocyanate has excellent strength, the alicyclic diisocyanate suppresses a scuff on the cover 12.

[0119] Specific examples of thermoplastic polyurethane elastomers include trade names "Elastollan NY80A", "Elastollan NY82A", "Elastollan NY84A", "Elastollan NY85A", "Elastollan NY88A", "Elastollan NY90A", "Elastollan NY97A", "Elastollan NY585", "Elastollan XKP016N", "Elastollan 1195ATR", "Elastollan ET890A", and "Elastollan ET88050", manufactured by BASF Japan Ltd.; and trade names "RESAMINE P4585LS" and "RESAMINE PS62490", manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd. From the standpoint that a low hardness of the cover 12 can be achieved, "Elastollan NY80A", "Elastollan NY82A", "Elastollan NY84A", "Elastollan NY85A", "Elastollan NY90A", and "Elastollan NY97A" are particularly preferred.

[0120] A thermoplastic polyurethane elastomer and another resin may be used in combination. Examples of the resin that can be used in combination include thermoplastic polyester elastomers, thermoplastic polyamide elastomers, thermoplastic polyolefin elastomers, styreneblock-containing thermoplastic elastomers, and ionomer resins. When a thermoplastic polyurethane elastomer and another resin are used in combination, the thermoplastic polyurethane elastomer is included as the principal component of the base polymer, in light of spin performance and scuff resistance. The proportion of the thermoplastic polyurethane elastomer to the entire base polymer is preferably equal to or greater than 50% by weight, more preferably equal to or greater than 70% by weight, and particularly preferably equal to or greater than 85% by weight.

[0121] According to need, a coloring agent such as titanium dioxide, a filler such as barium sulfate, a dispersant, an antioxidant, an ultraviolet absorber, a light stabilizer, a fluorescent material, a fluorescent brightener, and the like are included in the cover 12 in an adequate amount.

[0122] The cover 12 preferably has a Shore D hardness H_c of 48 or less. The golf ball 2 that includes the cover 12 having a hardness H_c of 48 or less has excellent controllability. In this respect, the hardness H_c is more preferably equal to or less than 40 and particularly preferably equal to or less than 32. In light of flight distance upon a shot with a driver, the hardness H_c is preferably equal to or greater than 10, more preferably equal to or greater than 15, and particularly preferably equal to or greater than 20. The hardness H_c is measured by the same measurement method as that for the hardness H_{m1} and the hardness H_{m2} .

[0123] The hardness H_c of the cover 12 is less than the hardness H_{m1} of the inner mid layer 6. When the golf ball 2 is hit with a driver, the sphere consisting of the core 4 and the inner mid layer 6 becomes significantly distorted since the head speed is high. Since this sphere has an outer-hard/inner-soft structure, the spin rate is suppressed. The hardness of the core 4 linearly changes. Thus, the golf ball 2 is launched at a high speed due to deformation and restoration of the core 4. The suppression of the spin rate and the high launch speed achieve a large flight distance. When the golf ball 2 is hit with a short iron, this sphere becomes less distorted since the head speed is low. When the golf ball 2 is hit with a short iron, the behavior of the golf ball 2 mainly depends on the cover 12. Since the cover 12 is flexible, a slip between the golf ball 2 and a clubface is suppressed. Due to the suppression of the slip, a high spin rate is obtained. The high spin rate achieves excellent controllability. In the golf ball 2, both desired flight performance upon a shot with a driver and desired controllability upon a shot with a short iron are achieved. In this respect, the hardness H_c is more preferably less than the hardness H_{m2} of the outer mid layer 8.

[0124] When the golf ball 2 is hit, the cover 12 including the polyurethane absorbs the shock. This absorption achieves soft feel at impact. Particularly, when the golf ball 2 is hit with a short iron or a putter, the cover 12 achieves excellent feel at impact.

[0125] In light of achievement of both desired flight performance and desired controllability, the difference ($H_{m1}-H_c$) between the hardness H_{m1} of the inner mid layer 6 and the hardness H_c of the cover 12 is preferably equal to or greater than 30, more preferably equal to or greater than 33, and particularly preferably equal to or greater than 35. The difference ($H_{m1}-H_c$) is preferably equal to or less than 45 and particularly preferably equal to or less than 40. In the golf ball 2 in which the hardness of the inner mid layer 6 and the hardness of the cover 12 meet this condition, a spin rate is suppressed upon a shot with a driver. In the golf ball 2, a backspin rate is high upon an approach shot.

[0126] Furthermore, in light of achievement of both desired flight performance and desired controllability, the difference ($H_{m2}-H_c$) between the hardness H_{m2} of the outer mid layer 8 and the hardness H_c of the cover 12 is preferably equal to or greater than 10 and particularly preferably equal to or greater than 18. The difference ($H_{m2}-H_c$) is preferably equal to or less than 30.

[0127] The cover 12 preferably has a JIS-C hardness less than the surface hardness H_s of the core 4. When the golf ball 2 is hit with a short iron, the flexible cover 12 is squeezed between the hard core 4 and the hard clubface. This

squeeze suppresses a slip of the golf ball 2 relative to the clubface. Due to the suppression of the slip, a high spin rate is obtained. The suppression of the slip suppresses variation of a spin rate. In light of suppression of a slip, the difference between the surface hardness Hs of the core 4 and the JIS-C hardness of the cover 12 is preferably equal to or greater than 30 and particularly preferably equal to or greater than 40.

5 **[0128]** In light of flight performance upon a shot with a driver, the cover 12 has a thickness Tc of preferably 0.8 mm or less and more preferably 0.6 mm or less. In light of durability and controllability, the thickness Tc is preferably equal to or greater than 0.3 mm and particularly preferably equal to or greater than 0.5 mm.

[0129] For forming the cover 12, known methods such as injection molding, compression molding, and the like can be used. When forming the cover 12, the dimples 14 are formed by pimples formed on the cavity face of a mold.

10 **[0130]** In light of achievement of both desired flight performance and desired controllability, the principal component of the base resin of the resin composition of the cover 12 is preferably a urethane resin or a urea resin, and the principal component of the base resin of the resin composition of the outer mid layer 8 is preferably an ionomer resin. In other words, the principal component of the base resin of the outer mid layer 8 is different from the principal component of the base resin of the cover 12.

15 **[0131]** In light of durability, the golf ball 2 that further includes the reinforcing layer 10 between the outer mid layer 8 and the cover 12 is preferred. The reinforcing layer 10 is positioned between the outer mid layer 8 and the cover 12. The reinforcing layer 10 firmly adheres to the outer mid layer 8 and also to the cover 12. The reinforcing layer 10 suppresses separation of the cover 12 from the outer mid layer 8. As described above, the cover 12 of the golf ball 2 is thin. When the golf ball 2 is hit by the edge of a clubface, a wrinkle is likely to occur. The reinforcing layer 10 suppresses occurrence of a wrinkle to improve the durability of the golf ball 2.

20 **[0132]** As the base polymer of the reinforcing layer 10, a two-component curing type thermosetting resin is suitably used. Specific examples of two-component curing type thermosetting resins include epoxy resins, urethane resins, acrylic resins, polyester resins, and cellulose resins. In light of strength and durability of the reinforcing layer 10, two-component curing type epoxy resins and two-component curing type urethane resins are preferred.

25 **[0133]** A two-component curing type epoxy resin is obtained by curing an epoxy resin with a polyamide type curing agent. Examples of epoxy resins used in two-component curing type epoxy resins include bisphenol A type epoxy resins, bisphenol F type epoxy resins, and bisphenol AD type epoxy resins. A bisphenol A type epoxy resin is obtained by a reaction of bisphenol A and an epoxy group-containing compound such as epichlorohydrin or the like. A bisphenol F type epoxy resin is obtained by a reaction of bisphenol F and an epoxy group-containing compound. A bisphenol AD type epoxy resin is obtained by a reaction of bisphenol AD and an epoxy group-containing compound. In light of balance among flexibility, chemical resistance, heat resistance, and toughness, bisphenol A type epoxy resins are preferred.

30 **[0134]** The polyamide type curing agent has a plurality of amino groups and one or more amide groups. The amino groups can react with epoxy groups. Specific examples of the polyamide type curing agent include polyamide amine curing agents and modified products thereof. A polyamide amine curing agent is obtained by a condensation reaction of a polymerized fatty acid and a polyamine. A typical polymerized fatty acid is obtained by heating and combining natural fatty acids including a large amount of unsaturated fatty acids, such as linoleic acid, linolenic acid, and the like, in the presence of a catalyst. Specific examples of unsaturated fatty acids include tall oil, soybean oil, linseed oil, and fish oil. A hydrogenated polymerized fatty acid having a dimer content of 90% by weight or greater and a trimer content of 10% by weight or less is preferred. Examples of preferable polyamines include polyethylene diamines, polyoxyalkylene di-
35 amines, and derivatives thereof.

40 **[0135]** In a mixture of an epoxy resin and a polyamide type curing agent, the ratio of the epoxy equivalent of the epoxy resin to the amine active hydrogen equivalent of the polyamide type curing agent is preferably equal to or greater than 1.0/1.4 but equal to or less than 1.0/1.0.

45 **[0136]** A two-component curing type urethane resin is obtained by a reaction of a base material and a curing agent. A two-component curing type urethane resin obtained by a reaction of a base material containing a polyol component and a curing agent containing a polyisocyanate or a derivative thereof, and a two-component curing type urethane resin obtained by a reaction of a base material containing an isocyanate group-terminated urethane prepolymer and a curing agent having active hydrogen, can be used. Particularly, a two-component curing type urethane resin obtained by a reaction of a base material containing a polyol component and a curing agent containing a polyisocyanate or a derivative thereof, is preferred.

50 **[0137]** As the polyol component of the base material, a urethane polyol is preferably used. The urethane polyol has urethane bonds and at least two or more hydroxyl groups. Preferably, the urethane polyol has hydroxyl groups at its ends. The urethane polyol can be obtained by causing a reaction of a polyol and a polyisocyanate at such a ratio that the hydroxyl groups of the polyol component are excessive in mole ratio with respect to the isocyanate groups of the polyisocyanate.

55 **[0138]** The polyol used for producing the urethane polyol has a plurality of hydroxyl groups. Polyols having a weight average molecular weight of 50 or greater but 2000 or less are preferred, and polyols having a weight average molecular weight of 100 or greater but 1000 or less are particularly preferred. Examples of low-molecular-weight polyols include

diols and triols. Specific examples of diols include ethylene glycol, diethylene glycol, triethylene glycol, 1,3-butanediol, 1,4-butanediol, neopentyl glycol, and 1,6-hexanediol. Specific examples of triols include trimethylol propane and hexanetriol. Examples of high-molecular-weight polyols include polyether polyols such as polyoxyethylene glycol (PEG), polyoxypropylene glycol (PPG), and polyoxytetramethylene glycol (PTMG); condensed polyester polyols such as polyethylene adipate (PEA), polybutylene adipate (PBA), and polyhexamethylene adipate (PHMA); lactone polyester polyols such as poly- ϵ -caprolactone (PCL); polycarbonate polyols such as polyhexamethylene carbonate; and acrylic polyols. Two or more polyols may be used in combination.

[0139] The polyisocyanate used for producing the urethane polyol has a plurality of isocyanate groups. Specific examples of the polyisocyanate include aromatic polyisocyanates such as 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, a mixture (TDI) of 2,4-toluene diisocyanate and 2,6-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate (MDI), 1,5-naphthylene diisocyanate (NDI), 3,3'-bitolylene-4,4'-diisocyanate (TODI), xylylene diisocyanate (XDI), tetramethylxylylene diisocyanate (TMXDI), and paraphenylene diisocyanate (PPDI); alicyclic polyisocyanates such as 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI), hydrogenated xylylene diisocyanate (H₆XDI), and isophorone diisocyanate (IPDI); and aliphatic polyisocyanates such as hexamethylene diisocyanate (HDI). Two or more of these polyisocyanates may be used in combination. In light of weather resistance, TMXDI, XDI, HDI, H₆XDI, IPDI, and H₁₂MDI are preferred.

[0140] In the reaction of the polyol and the polyisocyanate for producing the urethane polyol, a known catalyst can be used. A typical catalyst is dibutyl tin dilaurate.

[0141] In light of strength of the reinforcing layer 10, the proportion of the urethane bonds included in the urethane polyol is preferably equal to or greater than 0.1 mmol/g. In light of followability of the reinforcing layer 10 to the cover 12, the proportion of the urethane bonds included in the urethane polyol is preferably equal to or less than 5 mmol/g. The proportion of the urethane bonds can be adjusted by adjusting the molecular weight of the polyol, which is the material for the urethane polyol, and adjusting the blending ratio of the polyol and the polyisocyanate.

[0142] From the standpoint that the time taken for the reaction of the base material and the curing agent is short, the weight average molecular weight of the urethane polyol is preferably equal to or greater than 4000 and particularly preferably equal to or greater than 4500. In light of adhesion of the reinforcing layer 10, the weight average molecular weight of the urethane polyol is preferably equal to or less than 10000 and particularly preferably equal to or less than 9000.

[0143] In light of adhesion of the reinforcing layer 10, the hydroxyl value (mg KOH/g) of the urethane polyol is preferably equal to or greater than 15 and particularly preferably equal to or greater than 73. From the standpoint that the time taken for the reaction of the base material and the curing agent is short, the hydroxyl value of the urethane polyol is preferably equal to or less than 130 and particularly preferably equal to or less than 120.

[0144] The base material may contain, together with a urethane polyol, a polyol that does not have any urethane bond. The aforementioned polyol that is the material for the urethane polyol can be used in the base material. Polyols compatible with the urethane polyol are preferred. From the standpoint that the time taken for the reaction of the base material and the curing agent is short, the proportion of the urethane polyol in the base material on the solid content basis is preferably equal to or greater than 50% by weight and particularly preferably equal to or greater than 80% by weight. Ideally, the proportion is 100% by weight.

[0145] The curing agent contains a polyisocyanate or a derivative thereof. The aforementioned polyisocyanate that is the material for the urethane polyol can be used in the curing agent.

[0146] The reinforcing layer 10 may include additives such as a coloring agent (typically, titanium dioxide), a phosphate-based stabilizer, an antioxidant, a light stabilizer, a fluorescent brightener, an ultraviolet absorber, an anti-blocking agent, and the like. The additives may be added to the base material of the two-component curing type thermosetting resin, or may be added to the curing agent of the two-component curing type thermosetting resin.

[0147] The reinforcing layer 10 is obtained by applying, to the surface of the outer mid layer 8, a liquid that is prepared by dissolving or dispersing the base material and the curing agent in a solvent. In light of workability, application with a spray gun is preferred. After the application, the solvent is volatilized to permit a reaction of the base material with the curing agent, thereby forming the reinforcing layer 10. Examples of preferable solvents include toluene, isopropyl alcohol, xylene, methyl ethyl ketone, methyl isobutyl ketone, ethylene glycol monomethyl ether, ethylbenzene, propylene glycol monomethyl ether, isobutyl alcohol, and ethyl acetate.

[0148] In light of feel at impact, the golf ball 2 has an amount of compressive deformation Db of preferably 2.1 mm or greater, more preferably 2.2 mm or greater, and particularly preferably 2.3 mm or greater. In light of resilience performance, the amount of compressive deformation Db is preferably equal to or less than 3.2 mm, more preferably equal to or less than 3.0 mm, and particularly preferably equal to or less than 2.8 mm.

[0149] For measurement of the amount of compressive deformation, a YAMADA type compression tester is used. In the tester, a sphere (the golf ball 2, the core 4, or the like) is placed on a hard plate made of metal. Next, a cylinder made of metal gradually descends toward the sphere. The sphere, squeezed between the bottom face of the cylinder and the hard plate, becomes deformed. A migration distance of the cylinder, starting from the state in which an initial load of 98 N is applied to the sphere up to the state in which a final load of 1274 N is applied thereto, is measured.

[Second Embodiment - not claimed]

[0150] A golf ball 102 shown in FIG. 3 includes a spherical core 104, an inner mid layer 106 positioned outside the core 104, an outer mid layer 108 positioned outside the inner mid layer 106, a reinforcing layer 110 positioned outside the outer mid layer 108, and a cover 112 positioned outside the reinforcing layer 110. On the surface of the cover 112, a large number of dimples 114 are formed. Of the surface of the golf ball 102, a part other than the dimples 114 is a land 116. The golf ball 102 includes a paint layer and a mark layer on the external side of the cover 112, but these layers are not shown in the drawing.

[0151] The golf ball 102 has a diameter of 40 mm or greater but 45 mm or less. From the standpoint of conformity to the rules established by the United States Golf Association (USGA), the diameter is preferably equal to or greater than 42.67 mm. In light of suppression of air resistance, the diameter is preferably equal to or less than 44 mm and more preferably equal to or less than 42.80 mm. The golf ball 102 has a weight of 40 g or greater but 50 g or less. In light of attainment of great inertia, the weight is preferably equal to or greater than 44 g and more preferably equal to or greater than 45.00 g. From the standpoint of conformity to the rules established by the USGA, the weight is preferably equal to or less than 45.93 g.

[0152] FIG. 4 is a line graph showing a hardness distribution of the core 104 of the golf ball 102 in FIG. 3 according to the present invention. The horizontal axis of the graph indicates the ratio (%) of a distance from the central point of the core 104 to the radius of the core 104. The vertical axis of the graph indicates a JIS-C hardness. Nine measuring points obtained by dividing a region from the central point of the core 104 to the surface of the core 104 at intervals of 12.5% of the radius of the core 104 are plotted in the graph. The ratio of the distance from the central point of the core 104 to each of these measuring points to the radius of the core 104 is as follows.

First point: 0.0% (central point)

Second point: 12.5%

Third point: 25.0%

Fourth point: 37.5%

Fifth point: 50.0%

Sixth point: 62.5%

Seventh point: 75.0%

Eighth point: 87.5%

Ninth point: 100.0% (surface)

[0153] Hardnesses at the first to eighth points are measured by pressing a JIS-C type hardness scale against a cut plane of the core 104 that has been cut into two halves. A hardness at the ninth point is measured by pressing the JIS-C type hardness scale against the surface of the spherical core 104. For the measurement, an automated rubber hardness measurement machine (trade name "P1", manufactured by Kobunshi Keiki Co., Ltd.), to which this hardness scale is mounted, is used.

[0154] FIG. 4 also shows a linear approximation curve obtained by a least-square method on the basis of the distances and the hardnesses of the nine measuring points. In FIG. 4, the broken line does not greatly deviate from the linear approximation curve. In other words, the broken line has a shape close to the linear approximation curve. That is, in the core 104 according to the present invention, the hardness linearly increases from its central point toward its surface. When the golf ball 102 that includes the core 104 is hit with a driver, the energy loss is low. The core 104 has excellent resilience performance. When the golf ball 102 is hit with a driver, the flight distance is large. In the core 104, the hardness continuously increases from its central point toward its surface. In the core 104, there is no discontinuous point caused by a multilayer structure. When the golf ball 102 that includes the core 104 deforms by being hit, no local load is applied thereto. The golf ball 102 has excellent durability.

[0155] In the core 104, R^2 of the linear approximation curve obtained by the least-square method is equal to or greater than 0.95. R^2 is an index indicating the linearity of the broken line. For the core 104 for which R^2 is equal to or greater than 0.95, the shape of the broken line of the hardness distribution is close to a straight line. The core 104 for which R^2 is equal to or greater than 0.95 has excellent resilience performance. In this respect, R^2 is more preferably equal to or greater than 0.97 and particularly preferably equal to or greater than 0.99. R^2 is calculated by squaring a correlation coefficient R . The correlation coefficient R is calculated by dividing the covariance of the distance (%) from the central point and the hardness (JIS-C) by the standard deviation of the distance (%) from the central point and the standard deviation of the hardness (JIS-C).

[0156] The core 104 is obtained by crosslinking a rubber composition. The rubber composition includes:

(a) a base rubber;

(b) a co-crosslinking agent;

- (c) a crosslinking initiator; and
- (d) an acid and/or a salt.

5 **[0157]** The rubber composition of the core 104 can include the base rubber (a) described above for the core 4 of the first embodiment.

[0158] The co-crosslinking agent (b) is:

- (b1) an α,β -unsaturated carboxylic acid having 3 to 8 carbon atoms; and/or
- (b2) a metal salt of an α,β -unsaturated carboxylic acid having 3 to 8 carbon atoms.

10 The rubber composition of the core 104 can include the co-crosslinking agent (b) described above for the core 4 of the first embodiment.

15 **[0159]** The metal salt (b2) of the α,β -unsaturated carboxylic acid graft-polymerizes with the molecular chain of the base rubber, thereby crosslinking the rubber molecules. When the rubber composition includes the α,β -unsaturated carboxylic acid (b1), the rubber composition preferably further includes a metal compound (e). The metal compound (e) reacts with the α,β -unsaturated carboxylic acid (b1) in the rubber composition. A salt obtained by this reaction graft-polymerizes with the molecular chain of the base rubber. The rubber composition of the core 104 can include the metal compound (e) described above for the core 4 of the first embodiment.

20 **[0160]** In light of resilience performance of the golf ball 102, the amount of the co-crosslinking agent (b) is preferably equal to or greater than 15 parts by weight and particularly preferably equal to or greater than 20 parts by weight, per 100 parts by weight of the base rubber. In light of feel at impact, the amount is preferably equal to or less than 50 parts by weight, more preferably equal to or less than 45 parts by weight, and particularly preferably equal to or less than 40 parts by weight, per 100 parts by weight of the base rubber.

25 **[0161]** The rubber composition of the core 104 can include the crosslinking initiator (c) described above for the core 4 of the first embodiment. In light of resilience performance of the golf ball 102, the amount of the crosslinking initiator (c) is preferably equal to or greater than 0.2 parts by weight and particularly preferably equal to or greater than 0.5 parts by weight, per 100 parts by weight of the base rubber. In light of feel at impact and durability of the golf ball 102, the amount is preferably equal to or less than 5 parts by weight and particularly preferably equal to or less than 2.5 parts by weight, per 100 parts by weight of the base rubber.

30 **[0162]** The rubber composition of the core 104 can include the acid and/or the salt (d) described above for the core 4 of the first embodiment. The acid component included in the acid and/or the salt (d) has reactivity with a cationic component. During heating and forming of the core 104, the acid dissociates and reacts with the cationic component of the co-crosslinking agent (b). It is thought that the acid inhibits formation of the metal crosslinks by the co-crosslinking agent (b) in the central portion of the core 104. The acid component included in the salt exchanges the cationic component with the co-crosslinking agent (b). It is inferred that during heating and forming of the core 104, the salt breaks the metal crosslinks by the co-crosslinking agent (b) in the central portion of the core 104. In the present invention, the co-crosslinking agent (b) is not included in the concept of the acid and/or the salt (d).

35 **[0163]** From the standpoint that the hardness distribution of the core 104 is made appropriate, the amount of the acid and/or the salt (d) is preferably equal to or greater than 1.0 parts by weight, more preferably equal to or greater than 1.5 parts by weight, and even more preferably equal to or greater than 2 parts by weight, per 100 parts by weight of the base rubber. In light of resilience performance, the amount is preferably equal to or less than 40 parts by weight, more preferably equal to or less than 30 parts by weight, and particularly preferably equal to or less than 20 parts by weight, per 100 parts by weight of the base rubber.

40 **[0164]** The weight ratio of the co-crosslinking agent (b) and the acid and/or the salt (d) in the rubber composition is preferably equal to or greater than 3/7 but equal to or less than 9/1, and is particularly preferably equal to or greater than 4/6 but equal to or less than 8/2. From the rubber composition in which this weight ratio is within the above range, the core 104 whose hardness linearly increases from its central point toward its surface is obtained.

45 **[0165]** As the co-crosslinking agent (b), zinc acrylate is preferably used. Zinc acrylate whose surface is coated with stearic acid or zinc stearate for the purpose of improving dispersibility to rubber is present. When the rubber composition includes this zinc acrylate, the stearic acid or zinc stearate coating the zinc acrylate is not included in the concept of the acid and/or the salt (d).

50 **[0166]** The rubber composition of the core 104 preferably further includes the organic sulfur compound (f) described above for the core 4 of the first embodiment. The organic sulfur compound (f) can contribute to control of: the linearity of the hardness distribution of the core 104; and the degree of an outer-hard/inner-soft structure.

55 **[0167]** From the standpoint that the hardness distribution of the core 104 is made appropriate, the amount of the organic sulfur compound (f) is preferably equal to or greater than 0.05 parts by weight, more preferably equal to or greater than 0.1 parts by weight, and particularly preferably equal to or greater than 0.2 parts by weight, per 100 parts by weight of the base rubber. In light of resilience performance, the amount is preferably equal to or less than 5 parts

by weight, more preferably equal to or less than 3 parts by weight, and particularly preferably equal to or less than 1 parts by weight, per 100 parts by weight of the base rubber.

[0168] For the purpose of adjusting specific gravity and the like, a filler may be included in the core 104. Examples of suitable fillers include zinc oxide, barium sulfate, calcium carbonate, and magnesium carbonate. The amount of the filler is determined as appropriate so that the intended specific gravity of the core 104 is accomplished. A particularly preferable filler is zinc oxide. Zinc oxide serves not only as a specific gravity adjuster but also as a crosslinking activator.

[0169] According to need, an anti-aging agent, a coloring agent, a plasticizer, a dispersant, sulfur, a vulcanization accelerator, and the like are added to the rubber composition of the core 104. Crosslinked rubber powder or synthetic resin powder may also be dispersed in the rubber composition.

[0170] During heating and forming of the core 104, the heat of the crosslinking reaction of the base rubber remains near the central point of the core 104. Thus, during heating and forming of the core 104, the temperature at the central portion is high. The temperature gradually decreases from the central point toward the surface. The acid and/or the salt (d) reacts with a metal salt of the co-crosslinking agent (b) to break metal crosslinks. This reaction is accelerated in a region where the temperature is high. In other words, breaking of the metal crosslinks is likely to occur in the central portion of the core 104 where the temperature is high, and is unlikely to occur near the surface of the core 104. As a result, the crosslinking density of the core 104 increases from its central point toward its surface. In the core 104, the hardness linearly increases from its central point toward its surface. Further, since the rubber composition includes the organic sulfur compound (f) together with the acid and/or the salt (d), the gradient of the hardness distribution can be controlled, and the degree of the outer-hard/inner-soft structure of the core 104 can be increased.

[0171] In the present invention, a JIS-C hardness at a measuring point whose ratio of the distance from the central point of the core 104 to the radius of the core 104 is $x\%$ is represented by $H(x)$. The hardness at the central point of the core 104 is represented by $H(0.0)$. The surface hardness of the core 104 is represented by H_s . The difference ($H_s - H(0.0)$) between the surface hardness H_s and the central hardness $H(0.0)$ is equal to or greater than 15. The difference is great. In other words, the core 104 has an outer-hard/inner-soft structure. When the core 104 is hit with a driver, the recoil (torsional return) is great, and thus spin is suppressed. The core 104 contributes to the flight performance of the golf ball 102. In light of flight performance, the difference ($H_s - H(0.0)$) is more preferably equal to or greater than 25 and particularly preferably equal to or greater than 30. From the standpoint that the core 104 can easily be formed, the difference ($H_s - H(0.0)$) is preferably equal to or less than 50.

[0172] The hardness $H(0.0)$ at the central point of the core 104 is preferably equal to or greater than 40 but equal to or less than 70. The golf ball 102 that includes the core 104 having a hardness $H(0.0)$ of 40 or greater has excellent resilience performance. The hardness $H(0.0)$ is more preferably equal to or greater than 45 and particularly preferably equal to or greater than 50. In the core 104 having a hardness $H(0.0)$ of 70 or less, an outer-hard/inner-soft structure can be achieved. In the golf ball 102 that includes the core 104, spin can be suppressed. The hardness $H(0.0)$ is more preferably equal to or less than 68 and particularly preferably equal to or less than 65.

[0173] The hardness H_s at the surface of the core 104 is preferably equal to or greater than 78 but equal to or less than 96. In the core 104 having a hardness H_s of 78 or greater, an outer-hard/inner-soft structure can be achieved. In the golf ball 102 that includes the core 104, spin can be suppressed. The hardness H_s is more preferably equal to or greater than 80 and particularly preferably equal to or greater than 82. The golf ball 102 that includes the core 104 having a hardness H_s of 96 or less has excellent durability. The hardness H_s is more preferably equal to or less than 94 and particularly preferably equal to or less than 92.

[0174] The core 104 preferably has a diameter of 36.0 mm or greater. The core 104 having a diameter of 36.0 mm or greater can achieve excellent resilience performance of the golf ball 102. The core 104 having a diameter of 36.0 mm or greater can achieve an outer-hard/inner-soft structure of the golf ball 102. In this respect, the diameter is more preferably equal to or greater than 37.0 mm and particularly preferably equal to or greater than 38.0 mm. Furthermore, the diameter of the core 104 is preferably equal to or less than 40.0 mm. In the golf ball 102 that includes the core 104 having a diameter of 40.0 mm or less, the inner mid layer 106, the outer mid layer 108, and the cover 112 can have sufficient thicknesses. The golf ball 102 that includes the inner mid layer 106, the outer mid layer 108, and the cover 112 which have large thicknesses has excellent durability. In this respect, the diameter is particularly preferably equal to or less than 39.0 mm.

[0175] In light of feel at impact, the core 104 has an amount of compressive deformation D_c of preferably 3.0 mm or greater and particularly preferably 3.2 mm or greater. In light of resilience performance, the amount of compressive deformation D_c is preferably equal to or less than 3.8 mm and particularly preferably equal to or less than 3.5 mm.

[0176] For the inner mid layer 106, a resin composition is suitably used. Examples of the base resin of the resin composition include ionomer resins, polystyrenes, polyesters, polyamides, and polyolefins.

[0177] Particularly preferable base resins are ionomer resins. The golf ball 102 that includes the inner mid layer 106 including an ionomer resin has excellent resilience performance. An ionomer resin and another resin may be used in combination for the inner mid layer 106. In this case, the principal component of the base resin is preferably the ionomer resin. Specifically, the proportion of the ionomer resin to the entire base resin is preferably equal to or greater than 40%

by weight, more preferably equal to or greater than 60% by weight, and particularly preferably equal to or greater than 70% by weight.

[0178] The inner mid layer 106 can include the ionomer resin described above for the golf ball 2 of the first embodiment. The inner mid layer 106 can include the styrene block-containing thermoplastic elastomer described above for the golf ball 2 of the first embodiment.

[0179] According to need, a coloring agent such as titanium dioxide, a filler such as barium sulfate, a dispersant, an antioxidant, an ultraviolet absorber, a light stabilizer, a fluorescent material, a fluorescent brightener, and the like are included in the resin composition of the inner mid layer 106 in an adequate amount.

[0180] In light of flight performance, the inner mid layer 106 has a Shore D hardness Hm1 of preferably 30 or greater and more preferably 40 or greater. In the golf ball 102 that includes the inner mid layer 106 having a hardness Hm1 in this range, a spin rate is sufficiently suppressed upon a shot with a driver. The flight distance of the golf ball 102 is large. In light of controllability of the golf ball 102, the hardness Hm1 is preferably less than 50 and particularly preferably equal to or less than 47. When the golf ball 102 is hit with a short iron, the spin rate is high.

[0181] The Shore D hardness Hm1 of the inner mid layer 106 is measured according to the standards of "ASTM-D 2240-68" with a Shore D type hardness scale mounted to an automated rubber hardness measurement machine (trade name "P1", manufactured by Kobunshi Keiki Co., Ltd.). For the measurement, a slab that is formed by hot press and that has a thickness of about 2 mm is used. A slab kept at 23°C for two weeks is used for the measurement. At the measurement, three slabs are stacked. A slab formed from the same resin composition as the resin composition of the inner mid layer 106 is used.

[0182] The inner mid layer 106 preferably has a thickness T1 of 0.5 mm or greater but 1.6 mm or less. In light of durability, the thickness T1 is more preferably equal to or greater than 0.7 mm. In light of resilience performance, the thickness T1 is more preferably equal to or less than 1.2 mm.

[0183] For the outer mid layer 108, a resin composition is suitably used. Examples of the base resin of the resin composition include ionomer resins, polystyrenes, polyesters, polyamides, and polyolefins.

[0184] Particularly preferable base resins are ionomer resins. The golf ball 102 that includes the outer mid layer 108 including an ionomer resin has excellent resilience performance. An ionomer resin and another resin may be used in combination for the outer mid layer 108. In this case, the principal component of the base resin is preferably the ionomer resin. Specifically, the proportion of the ionomer resin to the entire base resin is preferably equal to or greater than 50% by weight, more preferably equal to or greater than 60% by weight, and particularly preferably equal to or greater than 70% by weight. The ionomer resin described above for the golf ball 2 of the first embodiment can also be used for the outer mid layer 108. The styrene block-containing thermoplastic elastomer described above for the golf ball 2 of the first embodiment may be used in combination for the outer mid layer 108.

[0185] As described later, the outer mid layer 108 has a hardness Hm2 greater than the hardness Hm1 of the inner mid layer 106. By decreasing the amount of the styrene block-containing thermoplastic elastomer included in the resin composition of the outer mid layer 108, a great hardness Hm2 can be achieved. By increasing the amount of a highly elastic resin in the resin composition, a great hardness Hm2 may be achieved. Specific examples of the highly elastic resin include polyamides.

[0186] According to need, a coloring agent such as titanium dioxide, a filler such as barium sulfate, a dispersant, an antioxidant, an ultraviolet absorber, a light stabilizer, a fluorescent material, a fluorescent brightener, and the like are included in the resin composition of the outer mid layer 108 in an adequate amount.

[0187] From the standpoint that an outer-hard/inner-soft structure is achieved in the sphere consisting of the core 104, the inner mid layer 106, and the outer mid layer 108, the outer mid layer 108 has a Shore D hardness Hm2 of preferably 55 or greater and more preferably 60 or greater. When the golf ball 102 is hit with a driver, the spin rate is low. The flight distance of the golf ball 102 is large. In light of controllability of the golf ball 102, the hardness Hm2 is preferably equal to or less than 70 and particularly preferably equal to or less than 68. When the golf ball 102 is hit with a short iron, the spin rate is high. The hardness Hm2 is measured by the same measurement method as that for the hardness Hm1.

[0188] From the standpoint that an outer-hard/inner-soft structure is achieved in the sphere consisting of the core 104, the inner mid layer 106, and the outer mid layer 108, the hardness Hm2 of the outer mid layer 108 is preferably greater than the hardness Hm1 of the inner mid layer 106. When the golf ball 102 that includes the sphere is hit with a driver, the spin rate is low. The flight distance of the golf ball 102 is large.

[0189] In light of resilience performance and controllability, the difference (Hm2-Hm1) between the hardness Hm2 of the outer mid layer 108 and the hardness Hm1 of the inner mid layer 106 is preferably equal to or greater than 10 and particularly preferably equal to or greater than 14. In light of flight performance, the difference (Hm2-Hm1) is preferably equal to or less than 30. When the golf ball 102 that includes the inner mid layer 106 and the outer mid layer 108 which have hardnesses in this range is hit with a driver, the spin rate is low. The flight distance of the golf ball 102 is large. When the golf ball 102 is hit with a short iron, the spin rate is high.

[0190] The outer mid layer 108 preferably has a thickness T2 of 0.5 mm or greater. In the golf ball 102 that includes the outer mid layer 108 having a thickness T2 of 0.5 mm or greater, the shock by a hit is alleviated. Thus, the golf ball

2 has excellent durability. In this respect, the thickness T2 is more preferably equal to or greater than 0.7 mm. The thickness T2 is preferably equal to or less than 1.6 mm. The golf ball 102 that includes the outer mid layer 108 having a thickness T2 of 1.6 mm or less includes a relatively large core 104. The golf ball 102 exerts sufficient resilience performance. In this respect, the thickness T2 is particularly preferably equal to or less than 1.2 mm.

5 **[0191]** The sum (T1+T2) of the thickness T1 and the thickness T2 is preferably equal to or greater than 1.0 mm. In the golf ball 102, the shock by a hit is alleviated. Thus, the golf ball 102 has excellent durability. In this respect, the sum (T1+T2) is more preferably equal to or greater than 1.3 mm. The sum (T1+T2) is preferably equal to or less than 3.0 mm. The golf ball 102 includes a relatively large core 104. The golf ball 102 exerts sufficient resilience performance. In this respect, the sum (T1+T2) is more preferably equal to or less than 2.0 mm.

10 **[0192]** For forming the outer mid layer 108, known methods such as injection molding, compression molding, and the like can be used.

15 **[0193]** For the cover 112, a resin composition is suitably used. A preferable base resin of the resin composition is a urethane resin or a urea resin. The principal component of the urethane resin is a polyurethane. The polyurethane is flexible. When the golf ball 102 that includes the cover 112 formed from the resin composition that includes the polyurethane is hit with a short iron, the spin rate is high. The cover 112 formed from this resin composition contributes to controllability upon a shot with a short iron. The polyurethane also contributes to the scuff resistance of the cover 112. Furthermore, the polyurethane can also contribute to excellent feel at impact when the golf ball 102 is hit with a putter or a short iron.

20 **[0194]** In light of ease of forming the cover 112, a preferable base resin is a thermoplastic polyurethane elastomer. The cover 112 can include the thermoplastic polyurethane elastomer described above for the golf ball 2 of the first embodiment. A thermoplastic polyurethane elastomer and another resin may be used in combination. Examples of the resin that can be used in combination include thermoplastic polyester elastomers, thermoplastic polyamide elastomers, thermoplastic polyolefin elastomers, styreneblock-containing thermoplastic elastomers, and ionomer resins. When a thermoplastic polyurethane elastomer and another resin are used in combination, the thermoplastic polyurethane elastomer is included as the principal component of the base polymer, in light of spin performance and scuff resistance. The proportion of the thermoplastic polyurethane elastomer to the entire base polymer is preferably equal to or greater than 50% by weight, more preferably equal to or greater than 70% by weight, and particularly preferably equal to or greater than 85% by weight.

25 **[0195]** According to need, a coloring agent such as titanium dioxide, a filler such as barium sulfate, a dispersant, an antioxidant, an ultraviolet absorber, a light stabilizer, a fluorescent material, a fluorescent brightener, and the like are included in the cover 112 in an adequate amount.

30 **[0196]** The cover 112 preferably has a Shore D hardness Hc of 48 or less. The golf ball 102 that includes the cover 112 having a hardness Hc of 48 or less has excellent controllability. In this respect, the hardness Hc is more preferably equal to or less than 40 and particularly preferably equal to or less than 32. In light of flight distance upon a shot with a driver, the hardness Hc is preferably equal to or greater than 10, more preferably equal to or greater than 15, and particularly preferably equal to or greater than 20. The hardness Hc is measured by the same measurement method as that for the hardness Hm1.

35 **[0197]** The hardness Hc of the cover 112 is less than the hardness Hm2 of the outer mid layer 108. When the golf ball 102 is hit with a driver, the sphere consisting of the core 104, the inner mid layer 106, and the outer mid layer 108 becomes significantly distorted since the head speed is high. Since this sphere has an outer-hard/inner-soft structure, the spin rate is suppressed. The hardness of the core 104 linearly changes. Thus, the golf ball 102 is launched at a high speed due to deformation and restoration of the core 104. The suppression of the spin rate and the high launch speed achieve a large flight distance. When the golf ball 102 is hit with a short iron, this sphere becomes less distorted since the head speed is low. When the golf ball 102 is hit with a short iron, the behavior of the golf ball 102 mainly depends on the cover 112. Since the cover 112 is flexible, a slip between the golf ball 102 and a clubface is suppressed. Due to the suppression of the slip, a high spin rate is obtained. The high spin rate achieves excellent controllability. In the golf ball 102, both desired flight performance upon a shot with a driver and desired controllability upon a shot with a short iron are achieved. In this respect, the hardness Hc is more preferably less than the hardness Hm1 of the inner mid layer 106.

40 **[0198]** When the golf ball 102 is hit, the cover 112 including the polyurethane absorbs the shock. This absorption achieves soft feel at impact. Particularly, when the golf ball 102 is hit with a short iron or a putter, the cover 112 achieves excellent feel at impact.

45 **[0199]** In light of achievement of both desired flight performance and desired controllability, the difference (Hm2-Hc) between the hardness Hm2 of the outer mid layer 108 and the hardness Hc of the cover 112 is preferably equal to or greater than 30, more preferably equal to or greater than 33, and particularly preferably equal to or greater than 36. The difference (Hm2-Hc) is preferably equal to or less than 45 and particularly preferably equal to or less than 40. In the golf ball 102 in which the hardness of the outer mid layer 108 and the hardness of the cover 112 meet this condition, a backspin rate is suppressed upon a shot with a driver. In the golf ball 102, a backspin rate is high upon an approach shot.

[0200] In light of achievement of both desired flight performance and desired controllability, the difference (Hm1-Hc) between the hardness Hm1 of the inner mid layer 106 and the hardness Hc of the cover 112 is preferably equal to or greater than 10 and particularly preferably equal to or greater than 15. The difference (Hm1-Hc) is preferably equal to or less than 22.

[0201] The cover 112 preferably has a JIS-C hardness less than the surface hardness Hs of the core 104. When the golf ball 102 is hit with a short iron, the flexible cover 112 is squeezed between the hard core 104 and the hard clubface. This squeeze suppresses a slip of the golf ball 102 relative to the clubface. Due to the suppression of the slip, a high spin rate is obtained. The suppression of the slip suppresses variation of a spin rate. In light of suppression of a slip, the difference between the surface hardness Hs of the core 104 and the JIS-C hardness of the cover 112 is preferably equal to or greater than 20 and particularly preferably equal to or greater than 27.

[0202] In light of flight performance upon a shot with a driver, the cover 112 has a thickness Tc of preferably 0.8 mm or less, more preferably 0.6 mm or less, and particularly preferably 0.4 mm or less. In light of durability and controllability, the thickness Tc is preferably equal to or greater than 0.2 mm and particularly preferably equal to or greater than 0.3 mm.

[0203] For forming the cover 112, known methods such as injection molding, compression molding, and the like can be used. When forming the cover 112, the dimples 114 are formed by pimples formed on the cavity face of a mold.

[0204] In light of achievement of both desired flight performance and desired controllability, the principal component of the base resin of the resin composition of the cover 112 is preferably a urethane resin or a urea resin, and the principal component of the base resin of the resin composition of the outer mid layer 108 is preferably an ionomer resin. In other words, the principal component of the base resin of the outer mid layer 108 is different from the principal component of the base resin of the cover 112.

[0205] In light of durability, the golf ball 102 that further includes the reinforcing layer 110 between the outer mid layer 108 and the cover 112 is preferred. The reinforcing layer 110 is positioned between the outer mid layer 108 and the cover 112. The reinforcing layer 110 firmly adheres to the outer mid layer 108 and also to the cover 112. The reinforcing layer 110 suppresses separation of the cover 112 from the outer mid layer 108. As described above, the cover 112 of the golf ball 102 is thin. When the golf ball 102 is hit by the edge of a clubface, a wrinkle is likely to occur. The reinforcing layer 110 suppresses occurrence of a wrinkle to improve the durability of the golf ball 102.

[0206] As the base polymer of the reinforcing layer 110, a two-component curing type thermosetting resin is suitably used. The reinforcing layer 110 can include the two-component curing type thermosetting resin described above for the golf ball 2 of the first embodiment. The reinforcing layer 110 may include additives such as a coloring agent (typically, titanium dioxide), a phosphate-based stabilizer, an antioxidant, a light stabilizer, a fluorescent brightener, an ultraviolet absorber, an anti-blocking agent, and the like. The additives may be added to the base material of the two-component curing type thermosetting resin, or may be added to the curing agent of the two-component curing type thermosetting resin.

[0207] The reinforcing layer 110 is obtained by applying, to the surface of the outer mid layer 108, a liquid that is prepared by dissolving or dispersing the base material and the curing agent in a solvent. In light of workability, application with a spray gun is preferred. After the application, the solvent is volatilized to permit a reaction of the base material with the curing agent, thereby forming the reinforcing layer 110. Examples of preferable solvents include toluene, isopropyl alcohol, xylene, methyl ethyl ketone, methyl isobutyl ketone, ethylene glycol monomethyl ether, ethylbenzene, propylene glycol monomethyl ether, isobutyl alcohol, and ethyl acetate.

[0208] In light of feel at impact, the golf ball 102 has an amount of compressive deformation Db of preferably 2.1 mm or greater, more preferably 2.2 mm or greater, and particularly preferably 2.3 mm or greater. In light of resilience performance, the amount of compressive deformation Db is preferably equal to or less than 3.2 mm, more preferably equal to or less than 3.0 mm, and particularly preferably equal to or less than 2.8 mm. The amount of compressive deformation is measured by the method described above for the golf ball 2 of the first embodiment.

[Third Embodiment]

[0209] A golf ball 202 shown in FIG. 5 includes a spherical core 204, an inner cover 206 positioned outside the core 204, a reinforcing layer 208 positioned outside the inner cover 206, an inner cover 210 positioned outside the reinforcing layer 208, and an outer cover 212 positioned outside the inner cover 210. On the surface of the outer cover 212, a large number of dimples 214 are formed. Of the surface of the golf ball 202, a part other than the dimples 214 is a land 216. The golf ball 202 includes a paint layer and a mark layer on the external side of the outer cover 212, but these layers are not shown in the drawing.

[0210] The golf ball 202 has a diameter of 40 mm or greater but 45 mm or less. From the standpoint of conformity to the rules established by the United States Golf Association (USGA), the diameter is preferably equal to or greater than 42.67 mm. In light of suppression of air resistance, the diameter is preferably equal to or less than 44 mm and more preferably equal to or less than 42.80 mm. The golf ball 202 has a weight of 40 g or greater but 50 g or less. In light of attainment of great inertia, the weight is preferably equal to or greater than 44 g and more preferably equal to or greater than 45.00 g. From the standpoint of conformity to the rules established by the USGA, the weight is preferably equal to

or less than 45.93 g.

[0211] FIG. 6 is a line graph showing a hardness distribution of the core 204 of the golf ball 202 in FIG. 5. The horizontal axis of the graph indicates the ratio (%) of a distance from the central point of the core 204 to the radius of the core 204. The vertical axis of the graph indicates a JIS-C hardness. Nine measuring points obtained by dividing a region from the central point of the core 204 to the surface of the core 204 at intervals of 12.5% of the radius of the core 204 are plotted in the graph. The ratio of the distance from the central point of the core 204 to each of these measuring points to the radius of the core 204 is as follows.

First point: 0.0% (central point)

Second point: 12.5%

Third point: 25.0%

Fourth point: 37.5%

Fifth point: 50.0%

Sixth point: 62.5%

Seventh point: 75.0%

Eighth point: 87.5%

Ninth point: 100.0% (surface)

Hardnesses at the first to eighth points are measured by pressing a JIS-C type hardness scale against a cut plane of the core 204 that has been cut into two halves. A hardness at the ninth point is measured by pressing the JIS-C type hardness scale against the surface of the spherical core 204. For the measurement, an automated rubber hardness measurement machine (trade name "P1", manufactured by Kobunshi Keiki Co., Ltd.), to which this hardness scale is mounted, is used.

[0212] FIG. 6 also shows a linear approximation curve obtained by a least-square method on the basis of the distances and the hardnesses of the nine measuring points. As is obvious from FIG. 6, the broken line of the hardness distribution does not greatly deviate from the linear approximation curve. In other words, the broken line has a shape close to the linear approximation curve. In the core 204, the hardness linearly increases from its central point toward its surface. When the core 204 is hit with a driver, the energy loss is low. The core 204 has excellent resilience performance. When the golf ball 202 is hit with a driver, the flight distance is large.

[0213] In the core 204, R^2 of the linear approximation curve obtained by the least-square method is equal to or greater than 0.95. R^2 is an index indicating the linearity of the broken line. For the core 204 for which R^2 is equal to or greater than 0.95, the shape of the broken line of the hardness distribution is close to a straight line. The core 204 for which R^2 is equal to or greater than 0.95 has excellent resilience performance. R^2 is more preferably equal to or greater than 0.96 and particularly preferably equal to or greater than 0.97. R^2 is calculated by squaring a correlation coefficient R . The correlation coefficient R is calculated by dividing the covariance of the distance (%) from the central point and the hardness (JIS-C) by the standard deviation of the distance (%) from the central point and the standard deviation of the hardness (JIS-C).

[0214] In the present invention, a JIS-C hardness at a measuring point whose ratio of the distance from the central point of the core 204 to the radius of the core 204 is $x\%$ is represented by $H(x)$. The hardness at the central point of the core 204 is represented by $H(0)$. The surface hardness of the core 204 is represented by H_s . The difference ($H_s - H(0)$) between the surface hardness H_s and the central hardness $H(0)$ is equal to or greater than 15. The difference is great. In other words, the core 204 has an outer-hard/inner-soft structure. When the core 204 is hit with a driver, the recoil (torsional return) is great, and thus spin is suppressed. The core 204 contributes to the flight performance of the golf ball 202. In light of flight performance, the difference ($H_s - H(0)$) is more preferably equal to or greater than 25 and particularly preferably equal to or greater than 30. From the standpoint that the core 204 can easily be formed, the difference ($H_s - H(0)$) is preferably equal to or less than 50.

[0215] The core 204 is obtained by crosslinking a rubber composition. The rubber composition includes:

(a) a base rubber;

(b) a co-crosslinking agent;

(c) a crosslinking initiator; and

(d) an acid and/or a salt.

[0216] During heating and forming of the core 204, the base rubber (a) is crosslinked by the co-crosslinking agent (b). The heat of the crosslinking reaction remains near the central point of the core 204. Thus, during heating and forming of the core 204, the temperature at the central portion is high. The temperature gradually decreases from the central point toward the surface. It is inferred that in the rubber composition, the acid reacts with a metal salt of the co-crosslinking agent (b) to bond to cation. It is inferred that in the rubber composition, the salt reacts with the metal salt of the co-crosslinking agent (b) to exchange cation. By the bonding and the exchange, metal crosslinks are broken. This breaking

is likely to occur in the central portion of the core 204 where the temperature is high, and is unlikely to occur near the surface of the core 204. As a result, the crosslinking density of the core 204 increases from its central point toward its surface. In the core 204, an outer-hard/inner-soft structure can be achieved. When the golf ball 202 that includes the core 204 is hit with a driver, the spin rate is low. The golf ball 202 achieves excellent flight performance upon a shot with a driver.

[0217] The rubber composition of the core 204 can include the base rubber (a) described above for the core 4 of the first embodiment.

[0218] The co-crosslinking agent (b) is:

(b1) an α,β -unsaturated carboxylic acid having 3 to 8 carbon atoms; and/or

(b2) a metal salt of an α,β -unsaturated carboxylic acid having 3 to 8 carbon atoms.

The rubber composition of the core 204 can include the co-crosslinking agent (b) described above for the core 4 of the first embodiment.

[0219] The metal salt (b2) of the α,β -unsaturated carboxylic acid graft-polymerizes with the molecular chain of the base rubber, thereby crosslinking the rubber molecules. When the rubber composition includes the α,β -unsaturated carboxylic acid (b1), the rubber composition preferably further includes a metal compound (e). The metal compound (e) reacts with the α,β -unsaturated carboxylic acid (b1) in the rubber composition. A salt obtained by this reaction graft-polymerizes with the molecular chain of the base rubber. The rubber composition of the core 204 can include the metal compound (e) described above for the core 4 of the first embodiment.

[0220] In light of resilience performance of the golf ball 202, the amount of the co-crosslinking agent (b) is preferably equal to or greater than 15 parts by weight and particularly preferably equal to or greater than 20 parts by weight, per 100 parts by weight of the base rubber. In light of feel at impact, the amount is preferably equal to or less than 50 parts by weight, more preferably equal to or less than 45 parts by weight, and particularly preferably equal to or less than 40 parts by weight, per 100 parts by weight of the base rubber.

[0221] The rubber composition of the core 204 can include the crosslinking initiator (c) described above for the core 4 of the first embodiment. In light of resilience performance of the golf ball 202, the amount of the crosslinking initiator (c) is preferably equal to or greater than 0.2 parts by weight and particularly preferably equal to or greater than 0.5 parts by weight, per 100 parts by weight of the base rubber. In light of feel at impact and durability of the golf ball 202, the amount is preferably equal to or less than 5.0 parts by weight and particularly preferably equal to or less than 2.5 parts by weight, per 100 parts by weight of the base rubber.

[0222] The rubber composition of the core 204 can include the acid and/or the salt (d) described above for the core 4 of the first embodiment. The co-crosslinking agent (b) is not included in the concept of the acid and/or the salt (d). It is inferred that during heating and forming of the core 204, the acid and/or the salt (d) breaks the metal crosslinks by the co-crosslinking agent (b) in the central portion of the core 204.

[0223] In light of linearity of the hardness distribution of the core 204, the amount of the acid and/or the salt (d) is preferably equal to or greater than 0.5 parts by weight, more preferably equal to or greater than 1.0 parts by weight, and particularly preferably equal to or greater than 2.0 parts by weight, per 100 parts by weight of the base rubber. In light of resilience performance, the amount is preferably equal to or less than 45 parts by weight, more preferably equal to or less than 40 parts by weight, and particularly preferably equal to or less than 30 parts by weight, per 100 parts by weight of the base rubber.

[0224] The weight ratio of the co-crosslinking agent (b) and the acid and/or the salt (d) in the rubber composition is preferably equal to or greater than 3/7 but equal to or less than 9/1, and is particularly preferably equal to or greater than 4/6 but equal to or less than 8/2. From the rubber composition in which this weight ratio is within the above range, the core 204 whose hardness linearly increases from its central point toward its surface can be obtained.

[0225] As the co-crosslinking agent (b), zinc acrylate is preferably used. Zinc acrylate whose surface is coated with stearic acid or zinc stearate for the purpose of improving dispersibility to rubber is present. In the present invention, when the rubber composition includes this zinc acrylate, this coating material is not included in the concept of the acid and/or the salt (d).

[0226] The rubber composition of the core 204 preferably further includes the organic sulfur compound (f) described above for the core 4 of the first embodiment. The organic sulfur compound (f) increases the linearity of the hardness distribution of the core 204. Furthermore, the organic sulfur compound (f) increases the degree of the outer-hard/inner-soft structure.

[0227] From the standpoint that the outer-hard/inner-soft structure of the core 204 can be achieved, the amount of the organic sulfur compound (f) is preferably equal to or greater than 0.05 parts by weight, more preferably equal to or greater than 0.1 parts by weight, and particularly preferably equal to or greater than 0.2 parts by weight, per 100 parts by weight of the base rubber. In light of resilience performance, the amount is preferably equal to or less than 5.0 parts by weight, more preferably equal to or less than 3.0 parts by weight, and particularly preferably equal to or less than 1.0

parts by weight, per 100 parts by weight of the base rubber.

[0228] For the purpose of adjusting specific gravity and the like, a filler may be included in the core 204. Examples of suitable fillers include zinc oxide, barium sulfate, calcium carbonate, and magnesium carbonate. The amount of the filler is determined as appropriate so that the intended specific gravity of the core 204 is accomplished. A particularly preferable filler is zinc oxide. Zinc oxide serves not only as a specific gravity adjuster but also as a crosslinking activator.

[0229] According to need, an anti-aging agent, a coloring agent, a plasticizer, a dispersant, sulfur, a vulcanization accelerator, and the like are added to the rubber composition of the core 204. Crosslinked rubber powder or synthetic resin powder may also be dispersed in the rubber composition.

[0230] The hardness $H(0)$ at the central point of the core 204 is preferably equal to or greater than 40 but equal to or less than 70. The golf ball 202 having a hardness $H(0)$ of 40 or greater has excellent resilience performance. In this respect, the hardness $H(0)$ is more preferably equal to or greater than 45 and particularly preferably equal to or greater than 50. In the core 204 having a hardness $H(0)$ of 70 or less, an outer-hard/inner-soft structure can be achieved. In the golf ball 202 that includes the core 204, spin can be suppressed. In this respect, the hardness $H(0)$ is more preferably equal to or less than 68 and particularly preferably equal to or less than 65.

[0231] The hardness H_s at the surface of the core 204 is preferably equal to or greater than 78 but equal to or less than 96. In the core 204 having a hardness H_s of 78 or greater, an outer-hard/inner-soft structure can be achieved. In the golf ball 202 that includes the core 204, spin can be suppressed. In this respect, the hardness H_s is more preferably equal to or greater than 80 and particularly preferably equal to or greater than 82. The golf ball 202 having a hardness H_s of 96 or less has excellent durability. In this respect, the hardness H_s is more preferably equal to or less than 94 and particularly preferably equal to or less than 92.

[0232] The core 204 preferably has a diameter of 38.0 mm or greater but 42.0 mm or less. The core 204 having a diameter of 38.0 mm or greater can achieve excellent resilience performance of the golf ball 202. In this respect, the diameter is more preferably equal to or greater than 39.0 mm and particularly preferably equal to or greater than 39.5 mm. In the golf ball 202 that includes the core 204 having a diameter of 42.0 mm or less, the mid layer 206, the inner cover 210, and the outer cover 212 can have sufficient thicknesses. The golf ball 202 that includes the mid layer 206, the inner cover 210, and the outer cover 212 which have large thicknesses has excellent durability. In this respect, the diameter is more preferably equal to or less than 41 mm and particularly preferably equal to or less than 40 mm. The core 204 may be hollow. The core 204 may have a rib on the surface thereof.

[0233] For the mid layer 206, a resin composition is suitably used. Examples of the base polymer of the resin composition include ionomer resins, polystyrenes, polyesters, polyamides, and polyolefins.

[0234] Particularly preferable base polymers are ionomer resins. The golf ball 202 that includes the mid layer 206 including an ionomer resin has excellent resilience performance. An ionomer resin and another resin may be used in combination for the mid layer 206. In this case, the principal component of the base polymer is preferably the ionomer resin. Specifically, the proportion of the ionomer resin to the entire base polymer is preferably equal to or greater than 50% by weight, more preferably equal to or greater than 60% by weight, and particularly preferably equal to or greater than 70% by weight.

[0235] The mid layer 206 can include the ionomer resin described above for the golf ball 2 of the first embodiment. The mid layer 206 can include the styrene block-containing thermoplastic elastomer described above for the golf ball 2 of the first embodiment.

[0236] The mid layer 206 may include a highly elastic resin as the base polymer. The highly elastic resin contributes to high rigidity of the mid layer 206. Specific examples of the highly elastic resin include polyamides.

[0237] According to need, a coloring agent such as titanium dioxide, a filler such as barium sulfate, a dispersant, an antioxidant, an ultraviolet absorber, a light stabilizer, a fluorescent material, a fluorescent brightener, and the like are included in the resin composition of the mid layer 206 in an adequate amount.

[0238] From the standpoint that an outer-hard/inner-soft structure can be achieved in the sphere consisting of the core 204 and the mid layer 206, the mid layer 206 has a Shore D hardness H_m of preferably 55 or greater and more preferably 60 or greater. In light of feel at impact of the golf ball 202, the hardness H_m is preferably equal to or less than 72 and particularly preferably equal to or less than 70. The hardness H_m is measured according to the standards of "ASTM-D 2240-68" with a Shore D type hardness scale mounted to an automated rubber hardness measurement machine (trade name "P1", manufactured by Kobunshi Keiki Co., Ltd.). For the measurement, a slab that is formed by hot press and that has a thickness of about 2 mm is used. A slab kept at 23°C for two weeks is used for the measurement. At the measurement, three slabs are stacked. A slab formed from the same resin composition as the resin composition of the mid layer 206 is used.

[0239] The mid layer 206 preferably has a thickness T_m of 0.5 mm or greater but 1.6 mm or less. In the sphere that includes the mid layer 206 having a thickness T_m of 0.5 mm or greater, the spin suppression effect provided by the outer-hard/inner-soft structure is great. In this respect, the thickness T_m is particularly preferably equal to or greater than 0.7 mm. The golf ball 202 that includes the mid layer 206 having a thickness T_m of 1.6 mm or less can include a large core 204. The large core 204 can contribute to the resilience performance of the golf ball 202. In this respect, the

thickness T_m is particularly preferably equal to or less than 1.2 mm.

[0240] For forming the mid layer 206, known methods such as injection molding, compression molding, and the like can be used.

[0241] For the inner cover 210, a resin composition is suitably used. A preferable base polymer of the resin composition is a polyurethane. The polyurethane is flexible. When the golf ball 202 that includes the inner cover 210 formed from the resin composition that includes the polyurethane is hit with a short iron, the spin rate is high. The inner cover 210 formed from this resin composition contributes to controllability upon a shot with a short iron. Furthermore, the polyurethane can also contribute to excellent feel at impact when the golf ball 202 is hit with a putter or a short iron.

[0242] In light of ease of forming the inner cover 210, a preferable base polymer is a thermoplastic polyurethane elastomer. The inner cover 210 can include the thermoplastic polyurethane elastomer described above for the golf ball 2 of the first embodiment. A thermoplastic polyurethane elastomer and another resin may be used in combination. Examples of the resin that can be used in combination include thermoplastic polyester elastomers, thermoplastic polyamide elastomers, thermoplastic polyolefin elastomers, styrene block-containing thermoplastic elastomers, and ionomer resins. When a thermoplastic polyurethane elastomer and another resin are used in combination, the thermoplastic polyurethane elastomer is included as the principal component of the base polymer, in light of spin performance. The proportion of the thermoplastic polyurethane elastomer to the entire base polymer is preferably equal to or greater than 50% by weight, more preferably equal to or greater than 70% by weight, and particularly preferably equal to or greater than 85% by weight.

[0243] According to need, a coloring agent such as titanium dioxide and a fluorescent pigment, a filler such as barium sulfate, a dispersant, an antioxidant, an ultraviolet absorber, a light stabilizer, a fluorescent material, a fluorescent brightener, and the like are included in the inner cover 210 in an adequate amount.

[0244] The inner cover 210 preferably has a Shore D hardness Hc_1 of 60 or less. The golf ball 202 that includes the inner cover 210 having a hardness Hc_1 of 60 or less has excellent controllability. In this respect, the hardness Hc_1 is more preferably equal to or less than 55 and particularly preferably equal to or less than 50. In light of flight distance upon a shot with a driver, the hardness Hc_1 is preferably equal to or greater than 40. The hardness Hc_1 is measured by the same measurement method as that for the hardness H_m .

[0245] The inner cover 210 preferably has a thickness T_1 of 0.1 mm or greater but 0.8 mm or less. The golf ball 202 having a thickness T_1 of 0.1 mm or greater has excellent controllability. In this respect, the thickness T_1 is more preferably equal to or greater than 0.2 mm and particularly preferably equal to or greater than 0.3 mm. The golf ball 202 having a thickness T_1 of 0.8 mm or less has excellent resilience performance. In this respect, the thickness T_1 is more preferably equal to or less than 0.6 mm and particularly preferably equal to or less than 0.5 mm.

[0246] For forming the inner cover 210, known methods such as injection molding, compression molding, and the like can be used.

[0247] For the outer cover 212, a resin composition is suitably used. A preferable base polymer of the resin composition is a polyurethane. The polyurethane is flexible. When the golf ball 202 that includes the outer cover 212 formed from the resin composition that includes the polyurethane is hit with a short iron, the spin rate is high. The outer cover 212 formed from this resin composition contributes to controllability upon a shot with a short iron. The polyurethane also contributes to the scuff resistance of the outer cover 212. Furthermore, the polyurethane can also contribute to excellent feel at impact when the golf ball 202 is hit with a putter or a short iron.

[0248] In light of ease of forming the outer cover 212, a preferable base polymer is a thermoplastic polyurethane elastomer. The outer cover 212 can include the thermoplastic polyurethane elastomer described above for the golf ball 2 of the first embodiment. Particularly, an elastomer that includes a polyurethane component obtained by a reaction of a polyol and an alicyclic diisocyanate is preferred. Since the alicyclic diisocyanate does not have any double bond in the main chain, the alicyclic diisocyanate suppresses yellowing of the outer cover 212. Furthermore, since the alicyclic diisocyanate has excellent strength, the alicyclic diisocyanate suppresses scuff on the outer cover 212.

[0249] From the standpoint that a low hardness of the outer cover 212 can be achieved, particularly preferable thermoplastic polyurethane elastomers are "Elastollan NY80A", "Elastollan NY82A", "Elastollan NY84A", "Elastollan NY85A", and "Elastollan NY90A".

[0250] A thermoplastic polyurethane elastomer and another resin may be used in combination. The outer cover 212 can include the resin described above for the inner cover 210. When a thermoplastic polyurethane elastomer and another resin are used in combination, the thermoplastic polyurethane elastomer is included as the principal component of the base polymer, in light of spin performance and scuff resistance. The proportion of the thermoplastic polyurethane elastomer to the entire base polymer is preferably equal to or greater than 50% by weight, more preferably equal to or greater than 70% by weight, and particularly preferably equal to or greater than 85% by weight.

[0251] According to need, a coloring agent such as titanium dioxide and a fluorescent pigment, a filler such as barium sulfate, a dispersant, an antioxidant, an ultraviolet absorber, a light stabilizer, a fluorescent material, a fluorescent brightener, and the like are included in the outer cover 212 in an adequate amount.

[0252] The outer cover 212 preferably has a Shore D hardness Hc_2 of 48 or less. The golf ball 202 that includes the

outer cover 212 having a hardness Hc2 of 48 or less has excellent controllability. In this respect, the hardness Hc2 is more preferably equal to or less than 40 and particularly preferably equal to or less than 32. In light of flight distance upon a shot with a driver, the hardness Hc2 is preferably equal to or greater than 10. The hardness Hc2 is measured by the same measurement method as that for the hardness Hm.

[0253] The outer cover 212 preferably has a thickness T2 of 0.1 mm or greater but 0.8 mm or less. The golf ball 202 having a thickness T2 of 0.1 mm or greater has excellent controllability. In this respect, the thickness T2 is more preferably equal to or greater than 0.2 mm and particularly preferably equal to or greater than 0.3 mm. The golf ball 202 having a thickness T2 of 0.8 mm or less has excellent resilience performance. In this respect, the thickness T2 is more preferably equal to or less than 0.6 mm and particularly preferably equal to or less than 0.5 mm.

[0254] For forming the outer cover 212, known methods such as injection molding, compression molding, and the like can be used. When forming the outer cover 212, the dimples 214 are formed by pimples formed on the cavity face of a mold.

[0255] The hardness Hm of the mid layer 206, the hardness Hc1 of the inner cover 210, and the hardness Hc2 of the outer cover 212 meet the relationships of the following mathematical formulas.

$$Hm > Hc1$$

$$Hm > Hc2$$

When the golf ball 202 is hit with a driver, the sphere consisting of the core 204 and the mid layer 206 becomes significantly distorted since the head speed is high. Since this sphere has an outer-hard/inner-soft structure, the spin rate is suppressed. The hardness of the core 204 linearly changes. Thus, the golf ball 202 is launched at a high speed due to deformation and restoration of the core 204. The suppression of the spin rate and the high launch speed achieve a large flight distance. When the golf ball 202 is hit with a short iron, this sphere becomes less distorted since the head speed is low. When the golf ball 202 is hit with a short iron, the behavior of the golf ball 202 mainly depends on the inner cover 210 and the outer cover 212. Since the inner cover 210 and the outer cover 212 are flexible, a slip between the golf ball 202 and a clubface is suppressed. Due to the suppression of the slip, a high spin rate is obtained. The high spin rate achieves excellent controllability. In the golf ball 202, both desired flight performance upon a shot with a driver and desired controllability upon a shot with a short iron are achieved.

[0256] When the golf ball 202 is hit, the inner cover 210 and the outer cover 212 absorb the shock. This absorption achieves soft feel at impact. Particularly, when the golf ball 202 is hit with a short iron or a putter, the inner cover 210 and the outer cover 212 achieve excellent feel at impact.

[0257] In light of achievement of both desired flight performance and desired controllability, the difference (Hm-Hc1) between the hardness Hm and the hardness Hc1 is preferably equal to or greater than 11, more preferably equal to or greater than 15, and particularly preferably equal to or greater than 18. The difference (Hm-Hc1) is preferably equal to or less than 40.

[0258] In light of achievement of both desired flight performance and desired controllability, the difference (Hm-Hc2) between the hardness Hm and the hardness Hc2 is preferably equal to or greater than 18, more preferably equal to or greater than 20, and particularly preferably equal to or greater than 36. The difference (Hm-Hc2) is preferably equal to or less than 60.

[0259] Preferably, the hardness Hc1 and the hardness Hc2 meet the relationship of the following mathematical formula.

$$Hc1 > Hc2$$

In the golf ball 202, the hardness decreases from the mid layer 206 via the inner cover 210 toward the outer cover 212. The golf ball 202 has excellent feel at impact.

[0260] In light of feel at impact, the difference (Hc1-Hc2) between the hardness Hc1 and the hardness Hc2 is preferably equal to or greater than 10 and particularly preferably equal to or greater than 15. The difference (Hc1-Hc2) is preferably equal to or less than 30.

[0261] The difference (T1-T2) between the thickness T1 of the inner cover 210 and the thickness T2 of the outer cover 212 is preferably equal to or greater than -0.4 mm but equal to or less than 0.4 mm. In the golf ball 202 in which the difference (T1-T2) is within the above range, the inner cover 210 and the outer cover 212 are easily formed. In this respect, the difference (T1-T2) is more preferably equal to or greater than -0.3 mm but equal to or less than 0.3 mm, and is particularly preferably equal to or greater than -0.2 mm but equal to or less than 0.2 mm.

[0262] In light of flight performance, the sum (T1+T2) of the thickness T1 of the inner cover 210 and the thickness T2

of the outer cover 212 is preferably equal to or less than 1.0 mm and particularly preferably equal to or less than 0.8 mm. In light of controllability, the sum (T1+T2) is preferably equal to or greater than 0.2 mm and particularly preferably equal to or greater than 0.4 mm.

[0263] The reinforcing layer 208 is positioned between the mid layer 206 and the inner cover 210. The reinforcing layer 208 firmly adheres to the mid layer 206 and also to the inner cover 210. The reinforcing layer 208 suppresses separation of the inner cover 210 from the mid layer 206.

[0264] As the base polymer of the reinforcing layer 208, a two-component curing type thermosetting resin is suitably used. The reinforcing layer 208 can include the two-component curing type thermosetting resin described above for the golf ball 2 of the first embodiment. The reinforcing layer 208 may include additives such as a coloring agent (typically, titanium dioxide), a phosphate-based stabilizer, an antioxidant, a light stabilizer, a fluorescent brightener, an ultraviolet absorber, an anti-blocking agent, and the like. The additives may be added to the base material of the two-component curing type thermosetting resin, or may be added to the curing agent of the two-component curing type thermosetting resin.

[0265] The reinforcing layer 208 is obtained by applying, to the surface of the mid layer 206, a liquid that is prepared by dissolving or dispersing the base material and the curing agent in a solvent. In light of workability, application with a spray gun is preferred. After the application, the solvent is volatilized to permit a reaction of the base material with the curing agent, thereby forming the reinforcing layer 208. Examples of preferable solvents include toluene, isopropyl alcohol, xylene, methyl ethyl ketone, methyl isobutyl ketone, ethylene glycol monomethyl ether, ethylbenzene, propylene glycol monomethyl ether, isobutyl alcohol, and ethyl acetate.

[0266] In light of feel at impact, the golf ball 202 has an amount of compressive deformation (comp'n) of preferably 2.3 mm or greater, more preferably 2.5 mm or greater, and particularly preferably 2.7 mm or greater. In light of resilience performance, the amount of compressive deformation is preferably equal to or less than 3.5 mm, more preferably equal to or less than 3.3 mm, and particularly preferably equal to or less than 3.1 mm. The amount of compressive deformation is measured by the method described above for the golf ball 2 of the first embodiment.

[Fourth Embodiment]

[0267] A golf ball 302 shown in FIG. 7 includes a spherical core 304, a mid layer 306 positioned outside the core 304, a reinforcing layer 308 positioned outside the mid layer 306, an inner cover 310 positioned outside the reinforcing layer 308, and an outer cover 312 positioned outside the inner cover 310. On the surface of the outer cover 312, a large number of dimples 314 are formed. Of the surface of the golf ball 302, a part other than the dimples 314 is a land 316. The golf ball 302 includes a paint layer and a mark layer on the external side of the outer cover 312, but these layers are not shown in the drawing.

[0268] The golf ball 302 has a diameter of 40 mm or greater but 45 mm or less. From the standpoint of conformity to the rules established by the United States Golf Association (USGA), the diameter is preferably equal to or greater than 42.67 mm. In light of suppression of air resistance, the diameter is preferably equal to or less than 44 mm and more preferably equal to or less than 42.80 mm. The golf ball 302 has a weight of 40 g or greater but 50 g or less. In light of attainment of great inertia, the weight is preferably equal to or greater than 44 g and more preferably equal to or greater than 45.00 g. From the standpoint of conformity to the rules established by the USGA, the weight is preferably equal to or less than 45.93 g.

[0269] FIG. 8 is a line graph showing a hardness distribution of the core 304 of the golf ball 302 in FIG. 7. The horizontal axis of the graph indicates the ratio (%) of a distance from the central point of the core 304 to the radius of the core 304. The vertical axis of the graph indicates a JIS-C hardness. Nine measuring points obtained by dividing a region from the central point of the core 304 to the surface of the core 304 at intervals of 12.5% of the radius of the core 304 are plotted in the graph. The ratio of the distance from the central point of the core 304 to each of these measuring points to the radius of the core 304 is as follows.

First point: 0.0% (central point)

Second point: 12.5%

Third point: 25.0%

Fourth point: 37.5%

Fifth point: 50.0%

Sixth point: 62.5%

Seventh point: 75.0%

Eighth point: 87.5%

Ninth point: 100.0% (surface)

Hardnesses at the first to eighth points are measured by pressing a JIS-C type hardness scale against a cut plane of the core 304 that has been cut into two halves. A hardness at the ninth point is measured by pressing the JIS-C type

hardness scale against the surface of the spherical core 304. For the measurement, an automated rubber hardness measurement machine (trade name "P1", manufactured by Kobunshi Keiki Co., Ltd.), to which this hardness scale is mounted, is used.

[0270] FIG. 8 also shows a linear approximation curve obtained by a least-square method on the basis of the distances and the hardnesses of the nine measuring points. As is obvious from FIG. 8, the broken line of the hardness distribution does not greatly deviate from the linear approximation curve. In other words, the broken line has a shape close to the linear approximation curve. In the core 304, the hardness linearly increases from its central point toward its surface. When the core 304 is hit with a driver, the energy loss is low. The core 304 has excellent resilience performance. When the golf ball 302 is hit with a driver, the flight distance is large.

[0271] In the core 304, R^2 of the linear approximation curve obtained by the least-square method is equal to or greater than 0.95. R^2 is an index indicating the linearity of the broken line. For the core 304 for which R^2 is equal to or greater than 0.95, the shape of the broken line of the hardness distribution is close to a straight line. The core 304 for which R^2 is equal to or greater than 0.95 has excellent resilience performance. R^2 is more preferably equal to or greater than 0.96 and particularly preferably equal to or greater than 0.97. R^2 is calculated by squaring a correlation coefficient R . The correlation coefficient R is calculated by dividing the covariance of the distance (%) from the central point and the hardness (JIS-C) by the standard deviation of the distance (%) from the central point and the standard deviation of the hardness (JIS-C).

[0272] In the present invention, a JIS-C hardness at a measuring point whose ratio of the distance from the central point of the core 304 to the radius of the core 304 is $x\%$ is represented by $H(x)$. The hardness at the central point of the core 304 is represented by $H(0)$. The surface hardness of the core 304 is represented by H_s . The difference ($H_s - H(0)$) between the surface hardness H_s and the central hardness $H(0)$ is equal to or greater than 15. The difference is great. In other words, the core 304 has an outer-hard/inner-soft structure. When the core 304 is hit with a driver, the recoil (torsional return) is great, and thus spin is suppressed. The core 304 contributes to the flight performance of the golf ball 302. In light of flight performance, the difference ($H_s - H(0)$) is more preferably equal to or greater than 25 and particularly preferably equal to or greater than 30. From the standpoint that the core 304 can easily be formed, the difference ($H_s - H(0)$) is preferably equal to or less than 50.

[0273] The core 304 is obtained by crosslinking a rubber composition. The rubber composition includes:

- (a) a base rubber;
- (b) a co-crosslinking agent;
- (c) a crosslinking initiator; and
- (d) an acid and/or a salt.

[0274] During heating and forming of the core 304, the base rubber (a) is crosslinked by the co-crosslinking agent (b). The heat of the crosslinking reaction remains near the central point of the core 304. Thus, during heating and forming of the core 304, the temperature at the central portion is high. The temperature gradually decreases from the central point toward the surface. It is inferred that in the rubber composition, the acid reacts with a metal salt of the co-crosslinking agent (b) to bond to cation. It is inferred that in the rubber composition, the salt reacts with the metal salt of the co-crosslinking agent (b) to exchange cation. By the bonding and the exchange, metal crosslinks are broken. This breaking is likely to occur in the central portion of the core 304 where the temperature is high, and is unlikely to occur near the surface of the core 304. As a result, the crosslinking density of the core 304 increases from its central point toward its surface. In the core 304, an outer-hard/inner-soft structure can be achieved. When the golf ball 302 that includes the core 304 is hit with a driver, the spin rate is low. The golf ball 302 achieves excellent flight performance upon a shot with a driver.

[0275] The rubber composition of the core 304 can include the base rubber (a) described above for the core 4 of the first embodiment.

[0276] The co-crosslinking agent (b) is:

- (b1) an α,β -unsaturated carboxylic acid having 3 to 8 carbon atoms; and/or
- (b2) a metal salt of an α,β -unsaturated carboxylic acid having 3 to 8 carbon atoms.

The rubber composition of the core 304 can include the co-crosslinking agent (b) described above for the core 4 of the first embodiment.

[0277] The metal salt (b2) of the α,β -unsaturated carboxylic acid graft-polymerizes with the molecular chain of the base rubber, thereby crosslinking the rubber molecules. When the rubber composition includes the α,β -unsaturated carboxylic acid (b1), the rubber composition preferably further includes a metal compound (e). The metal compound (e) reacts with the α,β -unsaturated carboxylic acid (b1) in the rubber composition. A salt obtained by this reaction graft-polymerizes with the molecular chain of the base rubber. The rubber composition of the core 304 can include the metal

compound (e) described above for the core 4 of the first embodiment.

[0278] In light of resilience performance of the golf ball 302, the amount of the co-crosslinking agent (b) is preferably equal to or greater than 15 parts by weight and particularly preferably equal to or greater than 20 parts by weight, per 100 parts by weight of the base rubber. In light of feel at impact, the amount is preferably equal to or less than 50 parts by weight, more preferably equal to or less than 45 parts by weight, and particularly preferably equal to or less than 40 parts by weight, per 100 parts by weight of the base rubber.

[0279] The rubber composition of the core 304 can include the crosslinking initiator (c) described above for the core 4 of the first embodiment. In light of resilience performance of the golf ball 302, the amount of the crosslinking initiator (c) is preferably equal to or greater than 0.2 parts by weight and particularly preferably equal to or greater than 0.5 parts by weight, per 100 parts by weight of the base rubber. In light of feel at impact and durability of the golf ball 302, the amount is preferably equal to or less than 5.0 parts by weight and particularly preferably equal to or less than 2.5 parts by weight, per 100 parts by weight of the base rubber.

[0280] The rubber composition of the core 304 can include the acid and/or the salt (d) described above for the core 4 of the first embodiment. The co-crosslinking agent (b) is not included in the concept of the acid and/or the salt (d). It is inferred that during heating and forming of the core 304, the acid and/or the salt (d) breaks the metal crosslinks by the co-crosslinking agent (b) in the central portion of the core 304.

[0281] In light of linearity of the hardness distribution of the core 304, the amount of the acid and/or the salt (d) is preferably equal to or greater than 0.5 parts by weight, more preferably equal to or greater than 1.0 parts by weight, and particularly preferably equal to or greater than 2.0 parts by weight, per 100 parts by weight of the base rubber. In light of resilience performance, the amount is preferably equal to or less than 40 parts by weight, more preferably equal to or less than 30 parts by weight, and particularly preferably equal to or less than 20 parts by weight, per 100 parts by weight of the base rubber.

[0282] The weight ratio of the co-crosslinking agent (b) and the acid and/or the salt (d) in the rubber composition is preferably equal to or greater than 3/7 but equal to or less than 9/1, and is particularly preferably equal to or greater than 4/6 but equal to or less than 8/2. From the rubber composition in which this weight ratio is within the above range, the core 304 whose hardness linearly increases from its central point toward its surface can be obtained.

[0283] As the co-crosslinking agent (b), zinc acrylate is preferably used. Zinc acrylate whose surface is coated with stearic acid or zinc stearate for the purpose of improving dispersibility to rubber is present. In the present invention, when the rubber composition includes this zinc acrylate, this coating material is not included in the concept of the acid and/or the salt (d).

[0284] The rubber composition of the core 304 preferably further includes the organic sulfur compound (f) described above for the core 4 of the first embodiment. The organic sulfur compound (f) increases the linearity of the hardness distribution of the core 304. Furthermore, the organic sulfur compound (f) increases the degree of the outer-hard/inner-soft structure.

[0285] From the standpoint that the outer-hard/inner-soft structure of the core 304 can be achieved, the amount of the organic sulfur compound (f) is preferably equal to or greater than 0.05 parts by weight, more preferably equal to or greater than 0.1 parts by weight, and particularly preferably equal to or greater than 0.2 parts by weight, per 100 parts by weight of the base rubber. In light of resilience performance, the amount is preferably equal to or less than 5.0 parts by weight, more preferably equal to or less than 3.0 parts by weight, and particularly preferably equal to or less than 1.0 parts by weight, per 100 parts by weight of the base rubber.

[0286] For the purpose of adjusting specific gravity and the like, a filler may be included in the core 304. Examples of suitable fillers include zinc oxide, barium sulfate, calcium carbonate, and magnesium carbonate. The amount of the filler is determined as appropriate so that the intended specific gravity of the core 304 is accomplished. A particularly preferable filler is zinc oxide. Zinc oxide serves not only as a specific gravity adjuster but also as a crosslinking activator.

[0287] According to need, an anti-aging agent, a coloring agent, a plasticizer, a dispersant, sulfur, a vulcanization accelerator, and the like are added to the rubber composition of the core 304. Crosslinked rubber powder or synthetic resin powder may also be dispersed in the rubber composition.

[0288] The hardness $H(0)$ at the central point of the core 304 is preferably equal to or greater than 40 but equal to or less than 70. The golf ball 302 having a hardness $H(0)$ of 40 or greater has excellent resilience performance. In this respect, the hardness $H(0)$ is more preferably equal to or greater than 45 and particularly preferably equal to or greater than 50. In the core 304 having a hardness $H(0)$ of 70 or less, an outer-hard/inner-soft structure can be achieved. In the golf ball 302 that includes the core 304, spin can be suppressed. In this respect, the hardness $H(0)$ is more preferably equal to or less than 68 and particularly preferably equal to or less than 65.

[0289] The hardness H_s at the surface of the core 304 is preferably equal to or greater than 78 but equal to or less than 96. In the core 304 having a hardness H_s of 78 or greater, an outer-hard/inner-soft structure can be achieved. In the golf ball 302 that includes the core 304, spin can be suppressed. In this respect, the hardness H_s is more preferably equal to or greater than 80 and particularly preferably equal to or greater than 82. The golf ball 302 having a hardness H_s of 96 or less has excellent durability. In this respect, the hardness H_s is more preferably equal to or less than 94 and

particularly preferably equal to or less than 92.

[0290] The core 304 preferably has a diameter of 38.0 mm or greater but 42.0 mm or less. The core 304 having a diameter of 38.0 mm or greater can achieve excellent resilience performance of the golf ball 302. In this respect, the diameter is more preferably equal to or greater than 39.0 mm and particularly preferably equal to or greater than 39.5 mm. In the golf ball 302 that includes the core 304 having a diameter of 42.0 mm or less, the mid layer 306, the inner cover 310, and the outer cover 312 can have sufficient thicknesses. The golf ball 302 that includes the mid layer 306, the inner cover 310, and the outer cover 312 which have large thicknesses has excellent durability. In this respect, the diameter is more preferably equal to or less than 41 mm and particularly preferably equal to or less than 40 mm. The core 304 may be hollow. The core 304 may have a rib on the surface thereof.

[0291] For the mid layer 306, a resin composition is suitably used. Examples of the base polymer of the resin composition include ionomer resins, polystyrenes, polyesters, polyamides, and polyolefins.

[0292] Particularly preferable base polymers are ionomer resins. The golf ball 302 that includes the mid layer 306 including an ionomer resin has excellent resilience performance. An ionomer resin and another resin may be used in combination for the mid layer 306. In this case, the principal component of the base polymer is preferably the ionomer resin. Specifically, the proportion of the ionomer resin to the entire base polymer is preferably equal to or greater than 50% by weight, more preferably equal to or greater than 60% by weight, and particularly preferably equal to or greater than 70% by weight.

[0293] The mid layer 306 can include the ionomer resin described above for the golf ball 2 of the first embodiment. The mid layer 306 can include the styrene block-containing thermoplastic elastomer described above for the golf ball 2 of the first embodiment.

[0294] The mid layer 306 may include a highly elastic resin as the base polymer. The highly elastic resin contributes to high rigidity of the mid layer 306. Specific examples of the highly elastic resin include polyamides.

[0295] According to need, a coloring agent such as titanium dioxide, a filler such as barium sulfate, a dispersant, an antioxidant, an ultraviolet absorber, a light stabilizer, a fluorescent material, a fluorescent brightener, and the like are included in the resin composition of the mid layer 306 in an adequate amount.

[0296] From the standpoint that an outer-hard/inner-soft structure can be achieved in the sphere consisting of the core 304 and the mid layer 306, the mid layer 306 has a Shore D hardness Hm of preferably 50 or greater, more preferably 55 or greater, and particularly preferably 58 or greater. In light of feel at impact of the golf ball 302, the hardness Hm is preferably equal to or less than 75, more preferably equal to or less than 72, and particularly preferably equal to or less than 70. The hardness Hm is measured according to the standards of "ASTM-D 2240-68" with a Shore D type hardness scale mounted to an automated rubber hardness measurement machine (trade name "P1", manufactured by Kobunshi Keiki Co., Ltd.). For the measurement, a slab that is formed by hot press and that has a thickness of about 2 mm is used. A slab kept at 23°C for two weeks is used for the measurement. At the measurement, three slabs are stacked. A slab formed from the same resin composition as the resin composition of the mid layer 306 is used.

[0297] The mid layer 306 preferably has a thickness Tm of 0.5 mm or greater but 1.6 mm or less. In the sphere that includes the mid layer 306 having a thickness Tm of 0.5 mm or greater, the spin suppression effect provided by the outer-hard/inner-soft structure is great. In this respect, the thickness Tm is particularly preferably equal to or greater than 0.7 mm. The golf ball 302 that includes the mid layer 306 having a thickness Tm of 1.6 mm or less can include a large core 304. The large core 304 can contribute to the resilience performance of the golf ball 302. In this respect, the thickness Tm is particularly preferably equal to or less than 1.2 mm.

[0298] For forming the mid layer 306, known methods such as injection molding, compression molding, and the like can be used.

[0299] For the inner cover 310, a resin composition is suitably used. A preferable base polymer of the resin composition is a polyurethane. The polyurethane is flexible. When the golf ball 302 that includes the inner cover 310 formed from the resin composition that includes the polyurethane is hit with a short iron, the spin rate is high. The inner cover 310 formed from this resin composition contributes to controllability upon a shot with a short iron. Furthermore, the polyurethane can also contribute to excellent feel at impact when the golf ball 302 is hit with a putter or a short iron.

[0300] In light of ease of forming the inner cover 310, a preferable base polymer is a thermoplastic polyurethane elastomer. The inner cover 310 can include the thermoplastic polyurethane elastomer described above for the golf ball 2 of the first embodiment.

[0301] From the standpoint that a low hardness of the inner cover 310 can be achieved, particularly preferable thermoplastic polyurethane elastomers are "Elastollan NY80A", "Elastollan NY82A", "Elastollan NY84A", "Elastollan NY85A", and "Elastollan NY90A".

[0302] A thermoplastic polyurethane elastomer and another resin may be used in combination. Examples of the resin that can be used in combination include thermoplastic polyester elastomers, thermoplastic polyamide elastomers, thermoplastic polyolefin elastomers, styreneblock-containing thermoplastic elastomers, and ionomer resins. When a thermoplastic polyurethane elastomer and another resin are used in combination, the thermoplastic polyurethane elastomer is included as the principal component of the base polymer, in light of spin performance. The proportion of the thermoplastic

polyurethane elastomer to the entire base polymer is preferably equal to or greater than 50% by weight, more preferably equal to or greater than 70% by weight, and particularly preferably equal to or greater than 85% by weight.

[0303] According to need, a coloring agent such as titanium dioxide and a fluorescent pigment, a filler such as barium sulfate, a dispersant, an antioxidant, an ultraviolet absorber, a light stabilizer, a fluorescent material, a fluorescent brightener, and the like are included in the inner cover 310 in an adequate amount.

[0304] The inner cover 310 preferably has a Shore D hardness Hc1 of 48 or less. The golf ball 302 that includes the inner cover 310 having a hardness Hc1 of 48 or less has excellent controllability. In this respect, the hardness Hc1 is more preferably equal to or less than 40 and particularly preferably equal to or less than 32. In light of flight distance upon a shot with a driver, the hardness Hc1 is preferably equal to or greater than 10. The hardness Hc1 is measured by the same measurement method as that for the hardness Hm.

[0305] The inner cover 310 preferably has a thickness T1 of 0.1 mm or greater but 0.8 mm or less. The golf ball 302 having a thickness T1 of 0.1 mm or greater has excellent controllability. In this respect, the thickness T1 is more preferably equal to or greater than 0.2 mm and particularly preferably equal to or greater than 0.3 mm. The golf ball 302 having a thickness T1 of 0.8 mm or less has excellent resilience performance. In this respect, the thickness T1 is more preferably equal to or less than 0.6 mm and particularly preferably equal to or less than 0.5 mm.

[0306] For forming the inner cover 310, known methods such as injection molding, compression molding, and the like can be used.

[0307] For the outer cover 312, a resin composition is suitably used. A preferable base polymer of the resin composition is a polyurethane. The polyurethane is flexible. When the golf ball 302 that includes the outer cover 312 formed from the resin composition that includes the polyurethane is hit with a short iron, the spin rate is high. The outer cover 312 formed from this resin composition contributes to controllability upon a shot with a short iron. The polyurethane also contributes to the scuff resistance of the outer cover 312. Furthermore, the polyurethane can also contribute to excellent feel at impact when the golf ball 302 is hit with a putter or a short iron.

[0308] In light of ease of forming the outer cover 312, a preferable base polymer is a thermoplastic polyurethane elastomer. The outer cover 312 can include the thermoplastic polyurethane elastomer described above for the golf ball 2 of the first embodiment. Particularly, an elastomer that includes a polyurethane component obtained by a reaction of a polyol and an alicyclic diisocyanate is preferred. Since the alicyclic diisocyanate does not have any double bond in the main chain, the alicyclic diisocyanate suppresses yellowing of the outer cover 312. Furthermore, since the alicyclic diisocyanate has excellent strength, the alicyclic diisocyanate suppresses scuff on the outer cover 312.

[0309] A thermoplastic polyurethane elastomer and another resin may be used in combination. The outer cover 312 can include the resin described above for the inner cover 310. When a thermoplastic polyurethane elastomer and another resin are used in combination, the thermoplastic polyurethane elastomer is included as the principal component of the base polymer, in light of spin performance and scuff resistance. The proportion of the thermoplastic polyurethane elastomer to the entire base polymer is preferably equal to or greater than 50% by weight, more preferably equal to or greater than 70% by weight, and particularly preferably equal to or greater than 85% by weight.

[0310] According to need, a coloring agent such as titanium dioxide and a fluorescent pigment, a filler such as barium sulfate, a dispersant, an antioxidant, an ultraviolet absorber, a light stabilizer, a fluorescent material, a fluorescent brightener, and the like are included in the outer cover 312 in an adequate amount.

[0311] The outer cover 312 preferably has a Shore D hardness Hc2 of 60 or less. The golf ball 302 that includes the outer cover 312 having a hardness Hc2 of 60 or less has excellent controllability. In this respect, the hardness Hc2 is more preferably equal to or less than 55 and particularly preferably equal to or less than 50. In light of flight distance upon a shot with a driver, the hardness Hc2 is preferably equal to or greater than 40. The hardness Hc2 is measured by the same measurement method as that for the hardness Hm.

[0312] The outer cover 312 preferably has a thickness T2 of 0.1 mm or greater but 0.8 mm or less. The golf ball 302 having a thickness T2 of 0.1 mm or greater has excellent controllability. In this respect, the thickness T2 is more preferably equal to or greater than 0.2 mm and particularly preferably equal to or greater than 0.3 mm. The golf ball 302 having a thickness T2 of 0.8 mm or less has excellent resilience performance. In this respect, the thickness T2 is more preferably equal to or less than 0.6 mm and particularly preferably equal to or less than 0.5 mm.

[0313] For forming the outer cover 312, known methods such as injection molding, compression molding, and the like can be used. When forming the outer cover 312, the dimples 314 are formed by pimples formed on the cavity face of a mold.

[0314] The hardness Hm of the mid layer 306 and the hardness Hc1 of the inner cover 310 meet the relationship of the following mathematical formula.

$$Hm > Hc1$$

Preferably, the hardness Hm of the mid layer 306 and the hardness Hc2 of the outer cover 312 meet the relationship of

the following mathematical formula.

$$H_m > H_{c2}$$

5

When the golf ball 302 is hit with a driver, the sphere consisting of the core 304 and the mid layer 306 becomes significantly distorted since the head speed is high. Since this sphere has an outer-hard/inner-soft structure, the spin rate is suppressed. The hardness of the core 304 linearly changes. Thus, the golf ball 302 is launched at a high speed due to deformation and restoration of the core 304. The suppression of the spin rate and the high launch speed achieve a large flight distance. When the golf ball 302 is hit with a short iron, this sphere becomes less distorted since the head speed is low. When the golf ball 302 is hit with a short iron, the behavior of the golf ball 302 mainly depends on the inner cover 310 and the outer cover 312. Since the inner cover 310 and the outer cover 312 are flexible, a slip between the golf ball 302 and a clubface is suppressed. Due to the suppression of the slip, a high spin rate is obtained. The high spin rate achieves excellent controllability. In the golf ball 302, both desired flight performance upon a shot with a driver and desired controllability upon a shot with a short iron are achieved.

10

15

[0315] When the golf ball 302 is hit, the inner cover 310 and the outer cover 312 absorb the shock. This absorption achieves soft feel at impact. Particularly, when the golf ball 302 is hit with a short iron or a putter, the inner cover 310 and the outer cover 312 achieve excellent feel at impact.

20

[0316] In light of achievement of both desired flight performance and desired controllability, the difference ($H_m - H_{c1}$) between the hardness H_m and the hardness H_{c1} is preferably equal to or greater than 18, more preferably equal to or greater than 20, and particularly preferably equal to or greater than 36. The difference ($H_m - H_{c1}$) is preferably equal to or less than 60.

25

[0317] In light of achievement of both desired flight performance and desired controllability, the difference ($H_m - H_{c2}$) between the hardness H_m and the hardness H_{c2} is preferably equal to or greater than 11, more preferably equal to or greater than 15, and particularly preferably equal to or greater than 18. The difference ($H_m - H_{c2}$) is preferably equal to or less than 40.

[0318] Preferably, the hardness H_{c1} and the hardness H_{c2} meet the relationship of the following mathematical formula.

30

$$H_{c2} > H_{c1}$$

When the golf ball 302 is hit with a driver, the spin rate is low. The golf ball 302 has excellent flight performance when being hit with a driver.

35

[0319] In light of flight performance, the difference ($H_{c2} - H_{c1}$) between the hardness H_{c2} and the hardness H_{c1} is preferably equal to or greater than 5 and particularly preferably equal to or greater than 10. The difference ($H_{c2} - H_{c1}$) is preferably equal to or less than 30.

40

[0320] The difference ($T_1 - T_2$) between the thickness T_1 of the inner cover 310 and the thickness T_2 of the outer cover 312 is preferably equal to or greater than -0.4 mm but equal to or less than 0.4 mm. In the golf ball 302 in which the difference ($T_1 - T_2$) is within the above range, the inner cover 310 and the outer cover 312 are easily formed. In this respect, the difference ($T_1 - T_2$) is more preferably equal to or greater than -0.3 mm but equal to or less than 0.3 mm, and is particularly preferably equal to or greater than -0.2 mm but equal to or less than 0.2 mm.

45

[0321] In light of flight performance, the sum ($T_1 + T_2$) of the thickness T_1 of the inner cover 310 and the thickness T_2 of the outer cover 312 is preferably equal to or less than 1.0 mm and particularly preferably equal to or less than 0.8 mm. In light of controllability, the sum ($T_1 + T_2$) is preferably equal to or greater than 0.2 mm and particularly preferably equal to or greater than 0.4 mm.

50

[0322] The reinforcing layer 308 is positioned between the mid layer 306 and the inner cover 310. The reinforcing layer 308 firmly adheres to the mid layer 306 and also to the inner cover 310. The reinforcing layer 308 suppresses separation of the inner cover 310 from the mid layer 306.

55

[0323] As the base polymer of the reinforcing layer 308, a two-component curing type thermosetting resin is suitably used. The reinforcing layer 308 can include the two-component curing type thermosetting resin described above for the golf ball 2 of the first embodiment. The reinforcing layer 308 may include additives such as a coloring agent (typically, titanium dioxide), a phosphate-based stabilizer, an antioxidant, a light stabilizer, a fluorescent brightener, an ultraviolet absorber, an anti-blocking agent, and the like. The additives may be added to the base material of the two-component curing type thermosetting resin, or may be added to the curing agent of the two-component curing type thermosetting resin.

[0324] The reinforcing layer 308 is obtained by applying, to the surface of the mid layer 306, a liquid that is prepared by dissolving or dispersing the base material and the curing agent in a solvent. In light of workability, application with a spray gun is preferred. After the application, the solvent is volatilized to permit a reaction of the base material with the

curing agent, thereby forming the reinforcing layer 308. Examples of preferable solvents include toluene, isopropyl alcohol, xylene, methyl ethyl ketone, methyl isobutyl ketone, ethylene glycol monomethyl ether, ethylbenzene, propylene glycol monomethyl ether, isobutyl alcohol, and ethyl acetate.

[0325] In light of feel at impact, the golf ball 302 has an amount of compressive deformation (comp'n) of preferably 2.3 mm or greater, more preferably 2.5 mm or greater, and particularly preferably 2.7 mm or greater. In light of resilience performance, the amount of compressive deformation is preferably equal to or less than 3.5 mm, more preferably equal to or less than 3.3 mm, and particularly preferably equal to or less than 3.1 mm. The amount of compressive deformation is measured by the method described above for the golf ball 2 of the first embodiment.

EXAMPLES

[Experiment 1]

[Example I-1]

[0326] A rubber composition was obtained by kneading 100 parts by weight of a high-cis polybutadiene (trade name "BR-730", manufactured by JSR Corporation), 38 parts by weight of zinc diacrylate (trade name "Sanceler SR", manufactured by SANSHIN CHEMICAL INDUSTRY CO., LTD.), 5 parts by weight of zinc oxide, an appropriate amount of barium sulfate, 0.2 parts by weight of 2-thionaphthol, 0.9 parts by weight of dicumyl peroxide (trade name "Percumyl D" manufactured by NOF Corporation), and 2 parts by weight of zinc octoate (a product of Mitsuwa Chemicals Co., Ltd.). This rubber composition was placed into a mold including upper and lower mold halves each having a hemispherical cavity, and heated at 170°C for 25 minutes to obtain a spherical core with a diameter of 38.5 mm. The amount of barium sulfate was adjusted such that the weight of a golf ball is 45.6 g.

[0327] A resin composition was obtained by kneading 55 parts by weight of an ionomer resin (the aforementioned "Surlyn 8945"), 45 parts by weight of another ionomer resin (the aforementioned "Himilan AM7329"), and 3 parts by weight of titanium dioxide with a twin-screw kneading extruder. The extruding conditions were a screw diameter of 45 mm, a screw rotational speed of 200 rpm, screw L/D of 35, and a die temperature of 160 to 230°C. The core was placed into a mold. The resin composition was injected around the core by injection molding to form an inner mid layer with a thickness of 0.8 mm.

[0328] A resin composition was obtained by kneading 27 parts by weight of an ionomer resin (the aforementioned "Surlyn 8945"), 45 parts by weight of another ionomer resin (the aforementioned "Himilan AM7329"), 28 parts by weight of a styrene block-containing thermoplastic elastomer (the aforementioned "Rabalon T3221C"), and 3 parts by weight of titanium dioxide with a twin-screw kneading extruder under the above extruding conditions. The sphere consisting of the core and the inner mid layer was placed into a mold. The resin composition was injected around the sphere by injection molding to form an outer mid layer with a thickness of 0.8 mm.

[0329] A paint composition (trade name "POLIN 750LE", manufactured by SHINTO PAINT CO., LTD.) including a two-component curing type epoxy resin as a base polymer was prepared. The base material liquid of this paint composition includes 30 parts by weight of a bisphenol A type solid epoxy resin and 70 parts by weight of a solvent. The curing agent liquid of this paint composition includes 40 parts by weight of a modified polyamide amine, 55 parts by weight of a solvent, and 5 parts by weight of titanium dioxide. The weight ratio of the base material liquid to the curing agent liquid is 1/1. This paint composition was applied to the surface of the outer mid layer with an air gun, and kept at 23°C for 12 hours to obtain a reinforcing layer with a thickness of 10 μm.

[0330] A resin composition was obtained by kneading 100 parts by weight of a thermoplastic polyurethane elastomer (the aforementioned "Elastollan NY82A"), 0.2 parts by weight of a hindered amine light stabilizer (trade name "TINUVIN 770", manufactured by Ciba Japan K.K.), 4 parts by weight of titanium dioxide, and 0.04 parts by weight of ultramarine blue with a twin-screw kneading extruder under the above extruding conditions. Half shells were formed from this resin composition by compression molding. The sphere consisting of the core, the inner mid layer, the outer mid layer, and the reinforcing layer was covered with two of these half shells. The sphere and the half shells were placed into a final mold that includes upper and lower mold halves each having a hemispherical cavity and that has a large number of pimples on its cavity face. A cover was obtained by compression molding. The thickness of the cover was 0.5 mm. Dimples having a shape that is the inverted shape of the pimples were formed on the cover. The surface of the cover was polished. A clear paint including a two-component curing type polyurethane as a base material was applied to this cover with an air gun, and was dried and cured to obtain a golf ball of Example I-1 with a diameter of 42.7 mm and a weight of 45.6 g.

[Examples 1-2 to 1-17 and Comparative Examples I-1 to I-6]

[0331] Golf balls of Examples 1-2 to 1-17 and Comparative Examples I-1 to I-6 were obtained in the same manner

EP 3 329 971 B1

as Example I-1, except the specifications of the core, the inner mid layer, the outer mid layer, and the cover were as shown in Tables 1-6 to I-10 below. The composition and hardness of the core are shown in detail in Tables I-1 to I-3 below. The compositions and hardnesses of the inner mid layer and the outer mid layer are shown in Table 1-4 below. The composition and hardness of the cover are shown in Table 1-5 below.

5

[Hit with Driver (W#1)]

[0332] A driver with a titanium head (trade name "XXIO", manufactured by DUNLOP SPORTS CO. LTD., shaft hardness: S, loft angle: 10.0°) was attached to a swing machine manufactured by True Temper Co. A golf ball was hit under the condition of a head speed of 45 m/sec. The spin rate was measured immediately after the hit. Furthermore, the flight distance from the launch point to the stop point was measured. The average value of data obtained by 10 measurements is shown in Tables 1-6 to I-10 below.

10

[Hit with Sand Wedge (SW)]

15

[0333] A sand wedge (trade name "XXIO", manufactured by DUNLOP SPORTS CO. LTD., shaft hardness: R, loft angle: 56.0°) was attached to a swing machine manufactured by True Temper Co. A golf ball was hit under the condition of a head speed of 21 m/sec. The backspin rate was measured immediately after the hit. The average value of data obtained by 10 measurements is shown in Tables 1-6 to I-10 below.

20

[Durability]

[0334] A driver with a titanium head (trade name "XXIO", manufactured by DUNLOP SPORTS CO. LTD., shaft hardness: S, loft angle: 10.0°) was attached to a swing robot M/C manufactured by True Temper Co. A golf ball having been kept at 23°C for 12 hours was used for the measurement. The golf ball was repeatedly hit under the condition of a head speed of 45 m/sec. The number of hits required to break the golf ball was measured. An index of the average value of data obtained for 12 golf balls is shown in Tables 1-6 to I-10 below. The higher the index is, the more excellent the durability of the golf ball is.

25

[Feel at Impact]

30

[0335] A golf player hit golf balls with a driver with a titanium head (trade name "XXIO", manufactured by DUNLOP SPORTS CO. LTD., shaft hardness: S, loft angle: 10.0°). The results of evaluation of feel at impact based on the following criteria are shown in Tables 1-6 to I-10 below.

35

- A: very favorable (soft)
- B: favorable (soft)
- C: slightly poor (slightly hard)
- D: poor (hard)

40

Table I-1 Composition and Hardness of Core (parts by weight)

Type	(1)	(2)	(3)	(4)	(5)
BR-730	100	100	100	100	100
Sanceler SR	34	38	38	38	39
ZN-DA90S	-	-	-	-	-
Zinc oxide	5	5	5	5	5
Barium sulfate	*	*	*	*	*
2-thionaphthol	0.2	0.2	0.2	0.2	0.2
Bis(pentabromophenyl)disulfide	-	-	-	-	-
Dicumyl peroxide	0.9	0.9	0.9	0.9	0.9
Zinc octoate	-	0.5	2	5	10
Zinc stearate	-	-	-	-	-

45

50

55

EP 3 329 971 B1

(continued)

Type	(1)	(2)	(3)	(4)	(5)
Zinc myristate	-	-	-	-	-
Amount of acid/salt	0	0.5	2	5	10
Vulcanization conditions					
Temperature (°C)	170	170	170	170	170
Time (min)	25	25	25	25	25
Hardness distribution (JIS-C hardness)					
H(0.0)	57.0	55.0	55.0	56.5	55.5
H(12.5)	68.0	65.5	62.0	59.5	59.0
H(25.0)	73.0	70.5	67.5	64.5	64.0
H(37.5)	74.0	72.0	69.5	67.0	67.0
H(50.0)	74.0	73.5	71.5	70.0	69.5
H(62.5)	74.0	75.0	72.5	74.0	72.0
H(75.0)	78.0	76.5	77.5	80.5	80.0
H(87.5)	82.0	81.5	82.5	85.0	84.0
Surface hardness Hs	87.0	86.0	86.5	89.0	87.0
* Appropriate amount					

Table I-2 Composition and Hardness of Core (parts by weight)

Type	(6)	(7)	(8)	(9)	(10)
BR-730	100	100	100	100	100
Sanceler SR	40	41	35	36	38
ZN-DA90S	-	-	-	-	-
Zinc oxide	5	5	5	5	5
Barium sulfate	*	*	*	*	*
2-thionaphthol	0.2	0.2	0.2	0.2	0.2
Bis(pentabromophenyl)disulfide	-	-	-	-	-
Dicumyl peroxide	0.9	0.9	0.9	0.9	0.9
Zinc octoate	30	45	-	-	-
Zinc stearate	-	-	10	20	-
Zinc myristate	-	-	-	-	5
Amount of acid/salt	30	45	10	20	5
Vulcanization conditions					
Temperature (°C)	170	170	170	170	170
Time (min)	25	25	25	25	25
Hardness distribution (JIS-C hardness)					
H(0.0)	53.5	64.0	57.5	56.0	57.0
H(12.5)	58.5	68.0	61.0	59.0	60.5

EP 3 329 971 B1

(continued)

	Hardness distribution (JIS-C hardness)					
5	H(25.0)	61.5	69.5	65.5	62.0	65.0
	H(37.5)	65.0	71.0	68.0	65.5	68.0
	H(50.0)	68.0	71.5	70.0	69.0	70.0
10	H(62.5)	70.5	72.5	71.5	71.0	72.0
	H(75.0)	73.5	73.5	81.0	80.0	80.5
	H(87.5)	76.0	76.0	85.0	82.0	85.0
	Surface hardness Hs	81.0	77.0	89.0	86.0	89.0
15	* Appropriate amount					

Table I-3 Composition and Hardness of Core (parts by weight)

	Type	(11)	(12)	(13)	(14)	(15)
20	BR-730	100	100	100	100	100
	Sanceler SR	39	40	-	39	37
	ZN-DA90S	-	-	38	-	-
25	Zinc oxide	5	5	5	5	5
	Barium sulfate	*	*	*	*	*
	2-thionaphthol	0.2	-	0.2	0.2	0.2
30	Bis(pentabromophenyl)disulfide	-	0.3	-	-	-
	Dicumyl peroxide	0.9	0.9	0.9	0.9	0.9
	Zinc octoate	-	5	5	5	5
	Zinc stearate	-	-	-	-	-
35	Zinc myristate	10	-	-	-	-
	Amount of acid/salt	10	5	5	5	5
	Vulcanization conditions					
40	Temperature (°C)	170	170	170	170	170
	Time (min)	25	25	25	25	25
	Hardness distribution (JIS-C hardness)					
45	H(0.0)	56.0	56.5	56.5	57.0	56.0
	H(12.5)	59.5	59.5	59.5	60.0	59.0
	H(25.0)	64.5	65.0	64.5	65.0	64.0
	H(37.5)	67.5	67.0	67.0	67.5	66.5
50	H(50.0)	69.5	70.0	71.0	70.5	69.5
	H(62.5)	72.0	74.0	74.0	74.5	73.5
	H(75.0)	80.5	80.0	80.5	81.0	80.0
	H(87.5)	84.5	85.0	85.0	85.5	84.5
55	Surface hardness Hs	87.5	89.0	89.0	89.5	88.5
	* Appropriate amount					

EP 3 329 971 B1

[0336] The details of the compounds listed in Tables I-1 to 1-3 are as follows.

BR730: a high-cis polybutadiene manufactured by JSR Corporation (cis-1, 4-bond content: 96% by weight, 1, 2-vinyl bond content: 1.3% by weight, Mooney viscosity (ML₁₊₄(100°C)): 55, molecular weight distribution (Mw/Mn): 3)
 Sanceler SR: zinc diacrylate manufactured by SANSHIN CHEMICAL INDUSTRY CO., LTD. (a product coated with 10% by weight of stearic acid)

ZN-DA90S: zinc diacrylate manufactured by Nihon Jyoryu Kogyo Co., Ltd. (a product coated with 10% by weight of zinc stearate)

Zinc oxide: trade name "Ginrei R" manufactured by Toho Zinc Co., Ltd.

Barium sulfate : trade name "Barium Sulfate BD" manufactured by Sakai Chemical Industry Co., Ltd.

2-thionaphthol: a product of Tokyo Chemical Industry Co., Ltd.

Bis(pentabromophenyl)disulfide: a product of Kawaguchi Chemical Industry Co., LTD.

Dicumyl peroxide: trade name "Percumyl D" manufactured by NOF Corporation

Zinc octoate: a product of Mitsuwa Chemicals Co., Ltd. (purity: 99% or greater)

Zinc stearate: a product of Wako Pure Chemical Industries, Ltd. (purity: 99% or greater)

Zinc myristate: a product of NOF Corporation (purity: 90% or greater)

Table I-4 Compositions and Hardnesses of Inner Mid Layer and Outer Mid Layer (parts by weight)

Type	a	b	c	d
Surlyn 8945	55	45	27	20
Himilan AM7329	45	45	45	25
Rabalon T3221C	-	10	28	55
Titanium dioxide	3	3	3	3
Hardness (Shore D)	65	56	48	29

Table I-5 Composition and Hardness of Cover (parts by weight)

Type	A	B	C	D
Elastollan NY82A	100	-	-	-
Elastollan NY85A	-	50	-	-
Elastollan NY90A	-	50	-	-
Elastollan NY97A	-	-	100	-
Surlyn 8945	-	-	-	40
Himilan AM7329	-	-	-	55
Rabalon T3221C	-	-	-	5
TINUVIN 770	0.2	0.2	0.2	0.2
Titanium dioxide	4	4	4	4
Ultramarine blue	0.04	0.04	0.04	0.04
Hardness Hc (Shore D)	29	36	47	60

Table I-6 Results of Evaluation

	Ex.I-1	Ex.I-2	Ex.I-3	Ex.I-4	Ex.I-5
Core Type	(3)	(4)	(5)	(6)	(7)
Diameter (mm)	38.5	38.5	38.5	38.5	38.5
Hs - H(0.0)	31.5	32.5	31.5	27.5	13.0

EP 3 329 971 B1

(continued)

5

10

15

20

25

30

35

40

	Ex.I-1	Ex.I-2	Ex.I-3	Ex.I-4	Ex.I-5
Core Type	(3)	(4)	(5)	(6)	(7)
R ²	0.96	0.99	0.99	0.99	0.95
Gradient	0.28	0.33	0.32	0.26	0.11
Inner mid layer					
Type	a	a	a	a	a
Hm1 (Shore D)	65	65	65	65	65
Diameter (mm)	40.1	40.1	40.1	40.1	40.1
T1 (mm)	0.8	0.8	0.8	0.8	0.8
Outer mid layer					
Type	c	c	c	c	c
Hm2 (Shore D)	48	48	48	48	48
Diameter (mm)	41.7	41.7	41.7	41.7	41.7
T2 (mm)	0.8	0.8	0.8	0.8	0.8
Cover Type	A	A	A	A	A
Hc (Shore D)	29	29	29	29	29
Tc (mm)	0.5	0.5	0.5	0.5	0.5
Hm1 - Hm2	17	17	17	17	17
Hm1 - Hc	36	36	36	36	36
T1 + T2 (mm)	1.6	1.6	1.6	1.6	1.6
Ball					
Db (mm)	2.6	2.6	2.6	2.6	2.6
(W#1) spin (rpm)	3200	3100	3150	3200	3280
(W#1) flight (m)	239	241	240	239	235
(SW) spin (rpm)	6850	6800	6800	6800	6850
Durability	110	115	113	110	103
Feel at impact	A	A	A	A	B

Table I-7 Results of Evaluation

45

50

55

	Ex.I-6	Ex.I-7	Ex.I-8	Ex.I-9	Ex.I-10
Core Type	(8)	(9)	(10)	(11)	(12)
Diameter (mm)	38.5	38.5	38.5	38.5	38.5
Hs - H(0.0)	31.5	30.0	32.0	31.5	32.5
R ²	0.97	0.98	0.97	0.98	0.99
Gradient	0.31	0.31	0.32	0.32	0.32
Inner mid layer					
Type	a	a	a	a	a
Hm1 (Shore D)	65	65	65	65	65

EP 3 329 971 B1

(continued)

5

10

15

20

25

30

35

Inner mid layer					
Type	a	a	a	a	a
Diameter (mm)	40.1	40.1	40.1	40.1	40.1
T1 (mm)	0.8	0.8	0.8	0.8	0.8
Outer mid layer					
Type	c	c	c	c	c
Hm2 (Shore D)	48	48	48	48	48
Diameter (mm)	41.7	41.7	41.7	41.7	41.7
T2 (mm)	0.8	0.8	0.8	0.8	0.8
Cover Type	A	A	A	A	A
Hc (Shore D)	29	29	29	29	29
Tc (mm)	0.5	0.5	0.5	0.5	0.5
Hm1 - Hm2	17	17	17	17	17
Hm1 - Hc	36	36	36	36	36
T1 + T2 (mm)	1.6	1.6	1.6	1.6	1.6
Ball					
Db (mm)	2.6	2.6	2.6	2.6	2.6
(W#1) spin (rpm)	3200	3150	3200	3150	3150
(W#1) flight (m)	239	240	238	239	240
(SW) spin (rpm)	6850	6800	6850	6800	6800
Durability	110	113	110	113	112
Feel at impact	A	A	A	A	A

Table I-8 Results of Evaluation

40

45

50

55

	Ex.I-11	Ex.I-12	Ex.I-13	Ex.I-14	Ex.I-15*
Core Type	(13)	(4)	(4)	(4)	(15)
Diameter (mm)	38.5	38.5	38.5	37.7	35.3
Hs - H(0.0)	32.5	32.5	32.5	32.5	32.5
R ²	0.99	0.99	0.99	0.99	0.99
Gradient	0.33	0.33	0.33	0.33	0.33
Inner mid layer					
Type	a	a	a	a	a
Hm1 (Shore D)	65	65	65	65	65
Diameter (mm)	40.1	40.1	40.1	39.3	38.5
T1 (mm)	0.8	0.8	0.8	0.8	1.6
Outer mid layer					
Type	c	c	c	c	c
Hm2 (Shore D)	48	48	48	48	48

EP 3 329 971 B1

(continued)

	Outer mid layer				
5	Type	c	c	c	c
	Diameter (mm)	41.7	41.7	41.7	40.9
	T2 (mm)	0.8	0.8	0.8	0.8
	Cover Type	A	B	C	A
10	Hc (Shore D)	29	36	47	29
	Tc (mm)	0.5	0.5	0.5	0.9
	Hm1 - Hm2	17	17	17	17
15	Hm1 - Hc	36	29	18	36
	T1 + T2 (mm)	1.6	1.6	1.6	1.6
	Ball				
	Db (mm)	2.6	2.6	2.6	2.6
20	(W#1) spin (rpm)	3100	3000	2950	3250
	(W#1) flight (m)	241	244	245	237
	(SW) spin (rpm)	6800	6650	6500	7000
25	Durability	115	112	107	115
	Feel at impact	A	A	B	A
	* not part of the invention				

Table I-9 Results of Evaluation

	Ex.I-16	Ex.I-17
Core Type	(4)	(14)
Diameter (mm)	38.5	38.5
Hs - H(0.0)	32.5	32.5
R ²	0.99	0.99
Gradient	0.33	0.33
Inner mid layer		
Type	a	a
Hm1 (Shore D)	65	65
Diameter (mm)	40.1	40.1
T1 (mm)	0.8	0.8
Outer mid layer		
Type	b	d
Hm2 (Shore D)	56	29
Diameter (mm)	41.7	41.7
T2 (mm)	0.8	0.8
Cover Type	A	A
Hc (Shore D)	29	29

EP 3 329 971 B1

(continued)

Outer mid layer		
Tc (mm)	0.5	0.5
Hm1 - Hm2	9	36
Hm1 - Hc	36	36
T1 + T2 (mm)	1.6	1.6
Ball		
Db (mm)	2.6	2.6
(W#1) spin (rpm)	3050	3200
(W#1) flight (m)	242	238
(SW) spin (rpm)	6650	6850
Durability	112	117
Feel at impact	B	A

Table I-10 Results of Evaluation

	Comp. Ex.I-1	Comp. Ex.I-2	Comp. Ex.I-3	Comp. Ex.I-4	Comp. Ex.I-5	Comp. Ex.I-6
Core Type	(1)	(4)	(15)	(15)	(14)	(2)
Diameter (mm)	38.5	38.5	38.5	38.5	38.5	38.5
Hs - H(0.0)	30.0	32.5	32.5	32.5	32.5	31.0
R ²	0.86	0.99	0.99	0.99	0.99	0.90
Gradient	0.23	0.33	0.33	0.33	0.33	0.25
Inner mid layer						
Type	a	c	b	a	c	a
Hm1 (Shore D)	65	48	56	65	48	65
Diameter (mm)	40.1	40.1	40.1	40.1	40.1	40.1
T1 (mm)	0.8	0.8	0.8	0.8	0.8	0.8
Outer mid layer						
Type	c	a	c	a	c	c
Hm2 (Shore D)	48	65	48	65	48	48
Diameter (mm)	41.7	41.7	41.7	41.7	41.7	41.7
T2 (mm)	0.8	0.8	0.8	0.8	0.8	0.8
Cover Type	A	A	D	A	A	A
Hc (Shore D)	29	29	60	29	29	29
Tc (mm)	0.5	0.5	0.5	0.5	0.5	0.5
Hm1 - Hm2	17	-17	8	0	0	17
Hm1 - Hc	36	19	-4	36	19	36
T1 + T2 (mm)	1.6	1.6	1.6	1.6	1.6	1.6
Ball						
Db (mm)	2.6	2.6	2.6	2.6	2.6	2.6

EP 3 329 971 B1

(continued)

Ball						
(W#1) spin (rpm)	3350	3000	2850	2900	3300	3300
(W#1) flight (m)	233	244	247	246	234	234
(SW) spin (rpm)	6850	6700	5800	6400	6900	6850
Durability	100	80	102	75	130	103
Feel at impact	B	C	C	D	B	B

[0337] As shown in Tables 1-6 to I-10, the golf balls according to Examples are excellent in various performance characteristics. From the results of evaluation, advantages of the present invention are clear.

[Experiment 2]

[Example II-1]

[0338] A rubber composition was obtained by kneading 100 parts by weight of a high-cis polybutadiene (trade name "BR-730", manufactured by JSR Corporation), 38 parts by weight of zinc diacrylate (trade name "Sanceler SR", manufactured by SANSHIN CHEMICAL INDUSTRY CO., LTD.), 5 parts by weight of zinc oxide, an appropriate amount of barium sulfate, 0.2 parts by weight of 2-thionaphthol, 0.9 parts by weight of dicumyl peroxide (trade name "Percumyl D" manufactured by NOF Corporation), and 2.0 parts by weight of zinc octoate (a product of Mitsuwa Chemicals Co., Ltd.). This rubber composition was placed into a mold including upper and lower mold halves each having a hemispherical cavity, and heated at 170°C for 25 minutes to obtain a spherical core with a diameter of 38.5 mm. The amount of barium sulfate was adjusted such that the weight of a golf ball is 45.6 g.

[0339] A resin composition was obtained by kneading 25 parts by weight of an ionomer resin (the aforementioned "Surlyn 8945"), 45 parts by weight of another ionomer resin (the aforementioned "Himilan AM7329"), 30 parts by weight of a styrene block-containing thermoplastic elastomer (the aforementioned "Rabalon T3221C"), and 3 parts by weight of titanium dioxide with a twin-screw kneading extruder. The extruding conditions were a screw diameter of 45 mm, a screw rotational speed of 200 rpm, screw L/D of 35, and a die temperature of 160 to 230°C. The core was placed into a mold. The resin composition was injected around the core by injection molding to form an inner mid layer with a thickness of 0.8 mm.

[0340] A resin composition was obtained by kneading 55 parts by weight of an ionomer resin (the aforementioned "Surlyn 8945"), 45 parts by weight of another ionomer resin (the aforementioned "Himilan AM7329"), and 3 parts by weight of titanium dioxide with a twin-screw kneading extruder under the above extruding conditions. The sphere consisting of the core and the inner mid layer was placed into a mold. The resin composition was injected around the sphere by injection molding to form an outer mid layer with a thickness of 0.8 mm.

[0341] A paint composition (trade name "POLIN 750LE", manufactured by SHINTO PAINT CO., LTD.) including a two-component curing type epoxy resin as a base polymer was prepared. The base material liquid of this paint composition includes 30 parts by weight of a bisphenol A type solid epoxy resin and 70 parts by weight of a solvent. The curing agent liquid of this paint composition includes 40 parts by weight of a modified polyamide amine, 55 parts by weight of a solvent, and 5 parts by weight of titanium dioxide. The weight ratio of the base material liquid to the curing agent liquid is 1/1. This paint composition was applied to the surface of the outer mid layer with an air gun, and kept at 23°C for 12 hours to obtain a reinforcing layer with a thickness of 6 μm.

[0342] A resin composition was obtained by kneading 100 parts by weight of a thermoplastic polyurethane elastomer (the aforementioned "Elastollan NY82A"), 0.2 parts by weight of a hindered amine light stabilizer (trade name "TINUVIN 770", manufactured by Ciba Japan K.K.), 4 parts by weight of titanium dioxide, and 0.04 parts by weight of ultramarine blue with a twin-screw kneading extruder under the above extruding conditions. Half shells were formed from this resin composition by compression molding. The sphere consisting of the core, the inner mid layer, the outer mid layer, and the reinforcing layer was covered with two of these half shells. The sphere and the half shells were placed into a final mold that includes upper and lower mold halves each having a hemispherical cavity and that has a large number of pimples on its cavity face. A cover was obtained by compression molding. The thickness of the cover was 0.5 mm. Dimples having a shape that is the inverted shape of the pimples were formed on the cover. The surface of the cover was polished. A clear paint including a two-component curing type polyurethane as a base material was applied to this cover with an air gun and was dried and cured to obtain a golf ball of Example II-1 with a diameter of 42.7 mm and a weight of 45.6 g.

EP 3 329 971 B1

[Examples II-2 to II-16 and Comparative Examples II-1 to II-7]

[0343] Golf balls of Examples II-2 to II-16 and Comparative Examples II-1 to II-7 were obtained in the same manner as Example II-1, except the specifications of the core, the inner mid layer, the outer mid layer, and the cover were as shown in Tables II-6 to II-11 below. The composition and hardness of the core are shown in detail in Tables II-1 to II-3 below. The compositions and hardnesses of the inner mid layer and the outer mid layer are shown in Table II-4 below. The composition and hardness of the cover are shown in Table II-5 below.

[Hit with Driver (W#1)]

[0344] A driver with a titanium head (trade name "XXIO", manufactured by DUNLOP SPORTS CO. LTD., shaft hardness: S, loft angle: 10.0°) was attached to a swing machine manufactured by True Temper Co. A golf ball was hit under the condition of a head speed of 45 m/sec. The spin rate was measured immediately after the hit. Furthermore, the flight distance from the launch point to the stop point was measured. The average value of data obtained by 10 measurements is shown in Tables II-6 to II-11 below.

[Hit with Sand Wedge (SW)]

[0345] A sand wedge (trade name "XXIO", manufactured by DUNLOP SPORTS CO. LTD., shaft hardness: R, loft angle: 56.0°) was attached to a swing machine manufactured by True Temper Co. A golf ball was hit under the condition of a head speed of 21 m/sec. The backspin rate was measured immediately after the hit. The average value of data obtained by 10 measurements is shown in Tables II-6 to II-11 below.

[Durability]

[0346] A driver with a titanium head (trade name "XXIO", manufactured by DUNLOP SPORTS CO. LTD., shaft hardness: S, loft angle: 10.0°) was attached to a swing robot M/C manufactured by True Temper Co. A golf ball having been kept at 23°C for 12 hours was used for the measurement. The golf ball was repeatedly hit under the condition of a head speed of 45 m/sec. The number of hits required to break the golf ball was measured. An index of the average value of data obtained for 12 golf balls is shown in Tables II-6 to II-11 below. The higher the index is, the more excellent the durability of the golf ball is.

Table II-1 Composition and Hardness of Core (parts by weight)

Type	(1)	(2)	(3)	(4)	(5)
BR-730	100	100	100	100	100
Sanceler SR	34	38	38	38	39
ZN-DA90S	-	-	-	-	-
Zinc oxide	5	5	5	5	5
Barium sulfate	*	*	*	*	*
2-thionaphthol	0.2	0.2	0.2	0.2	0.2
Bis(pentabromophenyl) disulfide	-	-	-	-	-
Dicumyl peroxide	0.9	0.9	0.9	0.9	0.9
Zinc octoate	-	0.5	2	5	10
Zinc stearate	-	-	-	-	-
Zinc myristate	-	-	-	-	-
Amount of acid/salt	0	0.5	2	5	10
Vulc. conditions					
Temperature (°C)	170	170	170	170	170
Time (min)	25	25	25	25	25

EP 3 329 971 B1

(continued)

	Hardness distribution (JIS-C hardness)					
5	H(0.0)	57.0	55.0	55.0	56.5	55.5
	H(12.5)	68.0	65.5	62.0	59.5	59.0
	H(25.0)	73.0	70.5	67.5	64.5	64.0
10	H(37.5)	74.0	72.0	69.5	67.0	67.0
	H(50.0)	74.0	73.5	71.5	70.0	69.5
	H(62.5)	74.0	75.0	72.5	74.0	72.0
	H(75.0)	78.0	76.5	77.5	80.5	80.0
15	H(87.5)	82.0	81.5	82.5	85.0	84.0
	Surface hardness Hs	87.0	86.0	86.5	89.0	87.0
	* Appropriate amount					

Table II-2 Composition and Hardness of Core (parts by weight)

	Type	(6)	(7)	(8)	(9)	(10)
	BR-730	100	100	100	100	100
25	Sanceler SR	40	41	35	36	38
	ZN-DA90S	-	-	-	-	-
	Zinc oxide	5	5	5	5	5
30	Barium sulfate	*	*	*	*	*
	2-thionaphthol	0.2	0.2	0.2	0.2	0.2
	Bis(pentabromophenyl)disulfide	-	-	-	-	-
	Dicumyl peroxide	0.9	0.9	0.9	0.9	0.9
35	Zinc octoate	30	45	-	-	-
	Zinc stearate	-	-	10	20	-
	Zinc myristate	-	-	-	-	5
40	Amount of acid/salt	30	45	10	20	5
	Vulc.conditions					
	Temperature (°C)	170	170	170	170	170
	Time (min)	25	25	25	25	25
45	Hardness distribution (JIS-C hardness)					
	H(0.0)	53.5	64.0	57.5	56.0	57.0
	H(12.5)	58.5	68.0	61.0	59.0	60.5
50	H(25.0)	61.5	69.5	65.5	62.0	65.0
	H(37.5)	65.0	71.0	68.0	65.5	68.0
	H(50.0)	68.0	71.5	70.0	69.0	70.0
	H(62.5)	70.5	72.5	71.5	71.0	72.0
55	H(75.0)	73.5	73.5	81.0	80.0	80.5
	H(87.5)	76.0	76.0	85.0	82.0	85.0

EP 3 329 971 B1

(continued)

Hardness distribution (JIS-C hardness)					
Surface hardness Hs	81.0	77.0	89.0	86.0	89.0
* Appropriate amount					

Table II-3 Composition and Hardness of Core (parts by weight)

Type	(11)	(12)	(13)	(14)	(15)
BR-730	100	100	100	100	100
Sanceler SR	39	40	-	39	37
ZN-DA90S	-	-	38	-	-
Zinc oxide	5	5	5	5	5
Barium sulfate	*	*	*	*	*
2-thionaphthol	0.2	-	0.2	0.2	0.2
Bis(pentabromophenyl)disulfide	-	0.3	-	-	-
Dicumyl peroxide	0.9	0.9	0.9	0.9	0.9
Zinc octoate	-	5	5	5	5
Zinc stearate	-	-	-	-	-
Zinc myristate	10	-	-	-	-
Amount of acid/salt	10	5	5	5	5
Vulc. conditions					
Temperature (°C)	170	170	170	170	170
Time (min)	25	25	25	25	25
Hardness distribution (JIS-C hardness)					
H(0.0)	56.0	56.5	56.5	57.0	56.0
H(12.5)	59.5	59.5	59.5	60.0	59.0
H(25.0)	64.5	65.0	64.5	65.0	64.0
H(37.5)	67.5	67.0	67.0	67.5	66.5
H(50.0)	69.5	70.0	71.0	70.5	69.5
H(62.5)	72.0	74.0	74.0	74.5	73.5
H(75.0)	80.5	80.0	80.5	81.0	80.0
H(87.5)	84.5	85.0	85.0	85.5	84.5
Surface hardness Hs	87.5	89.0	89.0	89.5	88.5
* Appropriate amount					

[0347] The details of the compounds listed in Tables II-1 to II-3 are as follows.

BR730: a high-cis polybutadiene manufactured by JSR Corporation (cis-1, 4-bond content: 96% by weight, 1, 2-vinyl bond content: 1.3% by weight, Mooney viscosity (ML₁₊₄(100°C)) : 55, molecular weight distribution (Mw/Mn): 3)
 Sanceler SR: zinc diacrylate manufactured by SANSHIN CHEMICAL INDUSTRY CO., LTD. (a product coated with 10% by weight of stearic acid)
 ZN-DA90S: zinc diacrylate manufactured by Nihon Jyoryu Kogyo Co., Ltd. (a product coated with 10% by weight of zinc stearate)

EP 3 329 971 B1

Zinc oxide: trade name "Ginrei R" manufactured by Toho Zinc Co., Ltd.

Barium sulfate : trade name "Barium Sulfate BD" manufactured by Sakai Chemical Industry Co., Ltd.

2-thionaphthol: a product of Tokyo Chemical Industry Co., Ltd.

Bis(pentabromophenyl)disulfide: a product of Kawaguchi Chemical Industry Co., LTD.

Dicumyl peroxide: trade name "Percumyl D" manufactured by NOF Corporation

Zinc octoate: a product of Mitsuwa Chemicals Co., Ltd. (purity: 99% or greater)

Zinc stearate: a product of Wako Pure Chemical Industries, Ltd. (purity: 99% or greater)

Zinc myristate: a product of NOF Corporation (purity: 90% or greater)

Table II-4 Compositions and Hardnesses of Inner Mid Layer and Outer Mid Layer (parts by weight)

Type	a	b	c	d
Surlyn 8945	55	45	25	20
Himilan AM7329	45	45	45	25
Rabalon T3221C	-	10	30	55
Titanium dioxide	3	3	3	3
Hardness (Shore D)	65	56	47	29

Table II-5 Composition and Hardness of Cover (parts by weight)

Type	A	B	C	D
Elastollan NY82A	100	-	-	-
Elastollan NY85A	-	50	-	-
Elastollan NY90A	-	50	-	-
Elastollan NY97A	-	-	100	-
Surlyn 8945	-	-	-	40
Himilan AM7329	-	-	-	55
Rabalon T3221C	-	-	-	5
TINUVIN 770	0.2	0.2	0.2	0.2
Titanium dioxide	4	4	4	4
Ultramarine blue	0.04	0.04	0.04	0.04
Hardness Hc (Shore D)	29	36	47	60

Table II-6 Results of Evaluation

	Ex.II-1	Ex.II-2	Ex.II-3	Ex.II-4
Core				
Type	(3)	(4)	(5)	(6)
Diameter (mm)	38.5	38.5	38.5	38.5
Hs - H(0.0)	31.5	32.5	31.5	27.5
R ²	0.96	0.99	0.99	0.99
Gradient	0.28	0.33	0.32	0.26

EP 3 329 971 B1

(continued)

	Inner mid layer				
5	Type	c	c	c	c
	Hm1 (Shore D)	47	47	47	47
	Diameter (mm)	40.1	40.1	40.1	40.1
	T1 (mm)	0.8	0.8	0.8	0.8
10	Outer mid layer				
	Type	a	a	a	a
	Hm2 (Shore D)	65	65	65	65
15	Diameter (mm)	41.7	41.7	41.7	41.7
	T2 (mm)	0.8	0.8	0.8	0.8
	Cover Type	A	A	A	A
	Hc (Shore D)	29	29	29	29
20	Tc (mm)	0.5	0.5	0.5	0.5
	Hm2 - Hm1	18	18	18	18
	Hm2 - Hc	36	36	36	36
25	T1 + T2 (mm)	1.6	1.6	1.6	1.6
	Ball				
	Db (mm)	2.6	2.6	2.6	2.6
	(W#1) spin (rpm)	3100	3000	3050	3100
30	(W#1) flight (m)	241	244	243	241
	(SW) spin (rpm)	6750	6700	6700	6700
	Durability	107	110	109	108

Table II-7 Results of Evaluation

		Ex.II-5	Ex.II-6	Ex.II-7	Ex.II-8
40	Core				
	Type	(7)	(8)	(9)	(10)
	Diameter (mm)	38.5	38.5	38.5	38.5
	Hs - H(0.0)	13.0	31.5	30.0	32.0
45	R ²	0.95	0.97	0.98	0.97
	Gradient	0.11	0.31	0.31	0.32
	Inner mid layer				
50	Type	c	c	c	c
	Hm1 (Shore D)	47	47	47	47
	Diameter (mm)	40.1	40.1	40.1	40.1
55	T1 (mm)	0.8	0.8	0.8	0.8

EP 3 329 971 B1

(continued)

5

10

15

20

25

Outer mid layer				
Type	a	a	a	a
Hm2 (Shore D)	65	65	65	65
Diameter (mm)	41.7	41.7	41.7	41.7
T2 (mm)	0.8	0.8	0.8	0.8
Cover Type	A	A	A	A
Hc (Shore D)	29	29	29	29
Tc (mm)	0.5	0.5	0.5	0.5
Hm2 - Hm1	18	18	18	18
Hm2 - Hc	36	36	36	36
T1 + T2 (mm)	1.6	1.6	1.6	1.6
Ball				
Db (mm)	2.6	2.6	2.6	2.6
(W#1) spin (rpm)	3300	3100	3050	3100
(W#1) flight(m)	234	241	243	240
(SW) spin (rpm)	6750	6750	6700	6750
Durability	104	107	109	107

30

35

40

45

50

55

Table II-8 Results of Evaluation

	Ex.II-9	Ex.II-10	Ex.II-11	Ex.II-12
Core				
Type	(11)	(12)	(13)	(14)
Diameter (mm)	38.5	38.5	38.5	38.5
Hs - H(0.0)	31.5	32.5	32.5	32.5
R ²	0.98	0.99	0.99	0.99
Gradient	0.32	0.32	0.33	0.33
Inner mid layer				
Type	c	c	c	c
Hm1 (Shore D)	47	47	47	47
Diameter (mm)	40.1	40.1	40.1	40.1
T1 (mm)	0.8	0.8	0.8	0.8
Outer mid layer				
Type	a	a	a	a
Hm2 (Shore D)	65	65	65	65
Diameter (mm)	41.7	41.7	41.7	41.7
T2 (mm)	0.8	0.8	0.8	0.8
Cover Type	A	A	A	B
Hc (Shore D)	29	29	29	36

EP 3 329 971 B1

(continued)

Outer mid layer				
Type	a	a	a	a
Tc (mm)	0.5	0.5	0.5	0.5
Hm2 - Hm1	18	18	18	18
Hm2 - Hc	36	36	36	29
T1 + T2 (mm)	1.6	1.6	1.6	1.6
Ball				
Db (mm)	2.6	2.6	2.6	2.6
(W#1) spin(rpm)	3050	3050	3000	2900
(W#1) flight(m)	242	243	244	246
(SW) spin (rpm)	6700	6700	6700	6550
Durability	109	108	110	108

Table II-9 Results of Evaluation

	Ex.II-13	Ex.II-14	Ex.II-15*	Ex.II-16
Core				
Type	(4)	(4)	(15)	(14)
Diameter (mm)	38.5	37.7	35.3	38.5
Hs - H(0.0)	32.5	32.5	32.5	32.5
R ²	0.99	0.99	0.99	0.99
Gradient	0.33	0.33	0.33	0.33
Inner mid layer				
Type	c	c	c	d
Hm1 (Shore D)	47	47	47	29
Diameter (mm)	40.1	39.3	38.5	40.1
T1 (mm)	0.8	0.8	1.6	0.8
Outer mid layer				
Type	a	a	a	a
Hm2 (Shore D)	65	65	65	65
Diameter (mm)	41.7	40.9	41.7	41.7
T2 (mm)	0.8	0.8	1.6	0.8
Cover Type	C	A	A	A
Hc (Shore D)	47	29	29	29
Tc (mm)	0.5	0.9	0.5	0.5
Hm2 - Hm1	18	18	18	36
Hm2 - Hc	18	36	36	36
T1 + T2 (mm)	1.6	1.6	3.2	1.6

EP 3 329 971 B1

(continued)

5

10

Ball				
Db (mm)	2.6	2.6	2.5	2.6
(W#1) spin (rpm)	2850	3150	3050	3100
(W#1) flight (m)	247	240	240	239
(SW) spin (rpm)	6400	6900	6600	6750
Durability	106	110	112	112
* not part of the invention				

15

Table II-10 Results of Evaluation

20

25

30

35

40

45

50

55

	Comp. Ex.II-1	Comp. Ex.II-2	Comp. Ex.II-3	Comp. Ex.II-4
Core				
Type	(1)	(2)	(4)	(4)
Diameter (mm)	38.5	38.5	38.5	38.5
Hs - H(0.0)	30.0	31.0	32.5	32.5
R ²	0.86	0.90	0.99	0.99
Gradient	0.23	0.25	0.33	0.33
Inner mid layer				
Type	c	c	b	a
Hm1 (Shore D)	47	47	56	65
Diameter (mm)	40.1	40.1	40.1	40.1
T1 (mm)	0.8	0.8	0.8	0.8
Outer mid layer				
Type	a	a	a	c
Hm2 (Shore D)	65	65	65	47
Diameter (mm)	41.7	41.7	41.7	41.7
T2 (mm)	0.8	0.8	0.8	0.8
Cover Type	A	A	A	A
Hc (Shore D)	29	29	29	29
Tc (mm)	0.5	0.5	0.5	0.5
Hm2 - Hm1	18	18	9	-18
Hm2 - Hc	36	36	36	18
T1 + T2 (mm)	1.6	1.6	1.6	1.6
Ball				
Db (mm)	2.6	2.6	2.5	2.6
(W#1) spin (rpm)	3250	3200	2950	3100
(W#1) flight (m)	235	237	245	241
(SW) spin (rpm)	6750	6750	6550	6800
Durability	100	103	109	120

EP 3 329 971 B1

Table II-11 Results of Evaluation

	Comp. Ex.II-5	Comp. Ex.II-6	Comp. Ex.II-7
Core			
Type	(15)	(15)	(14)
Diameter (mm)	38.5	38.5	38.5
Hs - H(0.0)	32.5	32.5	32.5
R ²	0.99	0.99	0.99
Gradient	0.33	0.33	0.33
Inner mid layer			
Type	c	a	c
Hm1 (Shore D)	47	65	47
Diameter (mm)	40.1	40.1	40.1
T1 (mm)	0.8	0.8	0.8
Outer mid layer			
Type	b	a	c
Hm2 (Shore D)	56	65	47
Diameter (mm)	41.7	41.7	41.7
T2 (mm)	0.8	0.8	0.8
Cover Type	D	A	A
Hc (Shore D)	60	29	29
Tc (mm)	0.5	0.5	0.5
Hm2 - Hm1	9	0	0
Hm2 - Hc	-4	36	18
T1 + T2 (mm)	1.6	1.6	1.6
Ball			
Db (mm)	2.6	2.6	2.6
(W#1) spin (rpm)	2750	2900	3350
(W#1) flight(m)	249	246	233
(SW) spin(rpm)	5700	6400	6950
Durability	103	85	128

[0348] As shown in Tables II-6 to II-11, the golf balls according to Examples are excellent in various performance characteristics. From the results of evaluation, advantages of the present invention are clear.

[Experiment 3]

[Example III-1]

[0349] A rubber composition was obtained by kneading 100 parts by weight of a high-cis polybutadiene (trade name "BR-730", manufactured by JSR Corporation), 36 parts by weight of zinc diacrylate (trade name "Sanceler SR", manufactured by SANSHIN CHEMICAL INDUSTRY CO., LTD.), 5 parts by weight of zinc oxide, an appropriate amount of barium sulfate, 0.32 parts by weight of 2-thionaphthol, 0.8 parts by weight of dicumyl peroxide, and 10 parts by weight of zinc stearate. This rubber composition was placed into a mold including upper and lower mold halves each having a

EP 3 329 971 B1

hemispherical cavity, and heated at 170°C for 25 minutes to obtain a core with a diameter of 39.5 mm. The amount of barium sulfate was adjusted such that the weight of a golf ball is 45.6 g.

[0350] A resin composition was obtained by kneading 55 parts by weight of an ionomer resin (the aforementioned "Surlyn 8945"), 45 parts by weight of another ionomer resin (the aforementioned "Himilan AM7329"), and 3 parts by weight of titanium dioxide with a twin-screw kneading extruder. The core was placed into a mold. The resin composition was injected around the core by injection molding to form a mid layer with a thickness of 1.0 mm.

[0351] A paint composition (trade name "POLIN 750LE", manufactured by SHINTO PAINT CO., LTD.) including a two-component curing type epoxy resin as a base polymer was prepared. The base material liquid of this paint composition includes 30 parts by weight of a bisphenol A type solid epoxy resin and 70 parts by weight of a solvent. The curing agent liquid of this paint composition includes 40 parts by weight of a modified polyamide amine, 55 parts by weight of a solvent, and 5 parts by weight of titanium dioxide. The weight ratio of the base material liquid to the curing agent liquid is 1/1. This paint composition was applied to the surface of the mid layer with a spray gun, and kept at 23°C for 12 hours to obtain a reinforcing layer with a thickness of 10 μm.

[0352] A resin composition was obtained by kneading 100 parts by weight of a thermoplastic polyurethane elastomer (the aforementioned "Elastollan NY97A"), 0.2 parts by weight of a hindered amine light stabilizer (trade name "TINUVIN 770", manufactured by Ciba Japan K.K.), 4 parts by weight of titanium dioxide, and 0.04 parts by weight of ultramarine blue with a twin-screw kneading extruder. Half shells were formed from this resin composition by compression molding. The sphere consisting of the core, the mid layer, and the reinforcing layer was covered with two of these half shells. The sphere and the half shells were placed into a mold including upper and lower mold halves each having a hemispherical cavity. An inner cover was obtained from the half shells by compression molding. The thickness of the inner cover was 0.3 mm.

[0353] A resin composition was obtained by kneading 100 parts by weight of a thermoplastic polyurethane elastomer (the aforementioned "Elastollan NY82A"), 0.2 parts by weight of a hindered amine light stabilizer (trade name "TINUVIN 770", manufactured by Ciba Japan K.K.), 4 parts by weight of titanium dioxide, and 0.04 parts by weight of ultramarine blue with a twin-screw kneading extruder. Half shells were formed from this resin composition by compression molding. The sphere consisting of the core, the mid layer, the reinforcing layer, and the inner cover was covered with two of these half shells. The sphere and the half shells were placed into a final mold that includes upper and lower mold halves each having a hemispherical cavity and that has a large number of pimples on its cavity face. An outer cover was obtained from the half shells by compression molding. The thickness of the outer cover was 0.3 mm. Dimples having a shape that is the inverted shape of the pimples were formed on the outer cover. A clear paint including a two-component curing type polyurethane as a base material was applied to this outer cover to obtain a golf ball of Example III-1 with a diameter of 42.7 mm.

[Examples III-2 to 111-21 and Comparative Examples III-1 to III-8]

[0354] Golf balls of Examples III-2 to 111-21 and Comparative Examples III-1 to III-8 were obtained in the same manner as Example III-1, except the specifications of the core, the mid layer, the inner cover, and the outer cover were as shown in Tables III-11 to 111-16 below. The composition of the core is shown in detail in Tables III-1 to III-3 below. The composition of the mid layer is shown in detail in Table III-4 below. The compositions of the inner cover and the outer cover are shown in detail in Table III-5 below. A hardness distribution of the core is shown in Tables III-6 to III-10 below.

[Comparative Example III-9]

[0355] A rubber composition was obtained by kneading 100 parts by weight of a high-cis polybutadiene (the aforementioned "BR-730"), 23 parts by weight of zinc diacrylate (the aforementioned "Sanceler SR"), 5 parts by weight of zinc oxide, an appropriate amount of barium sulfate, 0.5 parts by weight of bis (pentabromophenyl)disulfide, and 0.8 parts by weight of dicumyl peroxide. This rubber composition was placed into a mold including upper and lower mold halves each having a hemispherical cavity, and heated at 170°C for 25 minutes to obtain a center with a diameter of 25.0 mm. The amount of barium sulfate was adjusted such that the weight of a golf ball is 45.6 g.

[0356] A rubber composition was obtained by kneading 100 parts by weight of a high-cis polybutadiene (the aforementioned "BR-730"), 35.5 parts by weight of zinc diacrylate (the aforementioned "Sanceler SR"), 5 parts by weight of zinc oxide, an appropriate amount of barium sulfate, 0.5 parts by weight of bis (pentabromophenyl)disulfide, and 0.8 parts by weight of dicumyl peroxide. Half shells were formed from this rubber composition by compression molding. The center was covered with two of these half shells. The center and the half shells were placed into a mold including upper and lower mold halves each having a hemispherical cavity, and heated at 170°C for 25 minutes to obtain a core. An envelope layer was formed from the half shells. The diameter of the core was 39.5 mm. The core was covered with a mid layer, an inner cover, and an outer cover that are the same as in Example III-1. Furthermore, a clear paint that is the same as in Example III-1 was applied to the outer cover to obtain a golf ball of Comparative Example III-9 with a

EP 3 329 971 B1

diameter of 42.7 mm.

[Hit with Driver (W#1)]

5 **[0357]** A driver with a titanium head (trade name "XXIO", manufactured by DUNLOP SPORTS CO. LTD., shaft hardness: S, loft angle: 10.0°) was attached to a swing machine manufactured by True Temper Co. A golf ball was hit under the condition of a head speed of 45 m/sec. The spin rate was measured immediately after the hit. Furthermore, the distance from the launch point to the stop point was measured. The average value of data obtained by 10 measurements is shown in Tables III-11 to III-16 below.

10 [Hit with Sand Wedge (SW)]

15 **[0358]** A sand wedge (SW) was attached to the above swing machine. A golf ball was hit under the condition of a head speed of 21 m/sec. The backspin rate was measured immediately after the hit. The average value of data obtained by 10 measurements is shown in Tables III-11 to III-16 below.

[Durability]

20 **[0359]** A golf ball was kept at 23°C for 12 hours. The above driver was attached to the above swing machine. The golf ball was repeatedly hit under the condition of a head speed of 45 m/sec. The number of hits required to break the golf ball was counted. The average value of numbers of hits obtained by 12 measurements is shown as an index in Tables III-11 to III-16 below.

Table III-1 Composition of Core (parts by weight)

	A	B	C	D	E	F
BR-730	100	100	100	100	100	100
Sanceler SR	36	35	36	36	37	38
ZN-DA90S	-	-	-	-	-	-
Zinc oxide	5	5	5	5	5	5
Barium sulfate	*	*	*	*	*	*
2-thionaphthol	0.32	0.32	0.32	0.32	0.32	0.32
Bis(pentabromo phenyl) disulfide	-	-	-	-	-	-
Dicumyl peroxide	0.8	0.8	0.8	0.8	0.8	0.8
Zinc stearate	10.0	-	0.5	2.0	20.0	30.0
Zinc octoate	-	-	-	-	-	-
Zinc myristate	-	-	-	-	-	-
Acid/salt	10.0	0.0	0.5	2.0	20.0	30.0
* Appropriate amount						

Table III-2 Composition of Core (parts by weight)

	G	H	I	J	K
BR-730	100	100	100	100	100
Sanceler SR	39	39	40	39	40
ZN-DA90S	-	-	-	-	-
Zinc oxide	5	5	5	5	5
Barium sulfate	*	*	*	*	*
2-thionaphthol	0.32	0.32	0.32	0.32	0.32

EP 3 329 971 B1

(continued)

	G	H	I	J	K
Bis(pentabromo phenyl) disulfide	-	-	-	-	-
Dicumyl peroxide	0.8	0.8	0.8	0.8	0.8
Zinc stearate	45.0	-	-	-	-
Zinc octoate	-	5.0	10.0	-	-
Zinc myristate	-	-	-	5.0	10.0
Acid/salt	45.0	5.0	10.0	5.0	10.0
* Appropriate amount					

Table III-3 Composition of Core (parts by weight)

	L	M	N	P	Q
BR-730	100	100	100	100	100
Sanceler SR	39	-	37	23	35.5
ZN-DA90S	-	36	-	-	-
Zinc oxide	5	5	5	5	5
Barium sulfate	*	*	*	*	*
2-thionaphthol	-	0.32	0.32	-	-
Bis(pentabromo phenyl) disulfide	0.3	-	-	0.5	0.5
Dicumyl peroxide	0.8	0.8	0.8	0.8	0.8
Zinc stearate	10.0	10.0	10.0	-	-
Zinc octoate	-	-	-	-	-
Zinc myristate	-	-	-	-	-
Acid/salt	10.0	10.0	10.0	0.0	0.0
* Appropriate amount					

[0360] The details of the compounds listed in Tables III-1 to III-3 are as follows.

BR730: a high-cis polybutadiene manufactured by JSR Corporation (cis-1, 4-bond content: 96% by weight, 1, 2-vinyl bond content: 1.3% by weight, Mooney viscosity (ML₁₊₄(100°C)) : 55, molecular weight distribution (Mw/Mn): 3)
 Sanceler SR: zinc diacrylate manufactured by SANSHIN CHEMICAL INDUSTRY CO., LTD. (a product coated with 10% by weight of stearic acid)

ZN-DA90S: zinc diacrylate manufactured by Nihon Jyoryu Kogyo Co., Ltd. (a product coated with 10% by weight of zinc stearate)

Zinc oxide: trade name "Ginrei R" manufactured by Toho Zinc Co., Ltd.

Barium sulfate : trade name "Barium Sulfate BD" manufactured by Sakai Chemical Industry Co., Ltd.

2-thionaphthol: a product of Tokyo Chemical Industry Co., Ltd.

Bis(pentabromophenyl)disulfide: a product of Kawaguchi Chemical Industry Co., LTD.

Dicumyl peroxide: trade name "Percumyl D" manufactured by NOF Corporation

Zinc stearate: a product of Wako Pure Chemical Industries, Ltd.

Zinc octoate: a product of Mitsuwa Chemicals Co., Ltd.

Zinc myristate : a product of Wako Pure Chemical Industries, Ltd.

EP 3 329 971 B1

Table III-4 Composition of Mid Layer (parts by weight)

	M1	M2
Surlyn 8945	55	47
Himilan AM7329	45	45
Rabalon T3221C	-	8
Titanium dioxide	3	3
Hardness (Shore D)	65	58

Table III-5 Composition of Cover (parts by weight)

	C1	C2	C3	C4	C5	C6
Elastollan NY82A	100	-	-	-	-	60
Elastollan NY85A	-	50	-	-	-	40
Elastollan NY90A	-	50	-	-	5	-
Elastollan NY97A	-	-	100	-	95	-
Surlyn 8945	-	-	-	40	-	-
Himilan AM7329	-	-	-	55	-	-
Rabalon T3221C	-	-	-	5	-	-
TINUVIN 770	0.2	0.2	0.2	0.2	0.2	0.2
Titanium dioxide	4	4	4	4	4	4
Ultramarine blue	0.04	0.04	0.04	0.04	0.04	0.04
Hardness (Shore D)	29	36	47	60	46	30

Table III-6 Hardness Distribution

	Ex. III-1	Comp. Ex. III-1	Ex. III-2	Ex. III-3	Ex. III-4	Comp. Ex. III-2
Composition	A	C	D	E	F	G
H (0.0)	57.5	57.0	57.0	56.0	55.5	66.0
H(12.5)	61.0	67.5	62.5	59.0	60.5	69.0
H(25.0)	65.5	72.0	69.0	62.0	63.0	71.0
H(37.5)	68.0	73.0	70.5	65.5	66.0	72.0
H(50.0)	70.0	74.0	72.0	69.0	68.5	72.0
H(62.5)	71.5	74.5	73.0	71.0	70.0	73.0
H(75.0)	81.0	78.0	79.5	80.0	74.5	74.5
H(87.5)	85.0	82.5	83.5	82.0	77.0	77.0
Hs	89.0	88.0	88.5	86.0	83.0	79.0

Table III-7 Hardness Distribution

	Ex. 111-5	Ex. III-6	Ex. III-7	Ex. III-8	Ex. III-9	Ex. III-10
Composition	H	I	J	K	L	M
H (0.0)	56.5	55.5	57.0	56.0	60.0	57.0

EP 3 329 971 B1

(continued)

	Ex. 111-5	Ex. III-6	Ex. III-7	Ex. III-8	Ex. III-9	Ex. III-10
H(12.5)	59.5	59.0	60.5	59.5	62.5	61.0
H(25.0)	64.5	64.0	65.0	64.5	64.5	65.0
H(37.5)	67.0	67.0	68.0	67.5	67.5	67.5
H(50.0)	70.0	69.5	70.0	69.5	70.0	70.0
H(62.5)	72.0	72.0	72.0	72.0	71.5	73.0
H(75.0)	80.5	80.0	80.5	80.5	80.0	80.5
H(87.5)	85.0	84.0	85.0	84.5	83.0	85.0
Hs	89.0	87.0	89.0	87.5	87.0	89.0

Table III-8 Hardness Distribution

	Ex. III-11	Ex. III-12	Ex. III-13	Ex. III-14	Ex. III-15	Ex. III-16
Composition	N	A	A	A	A	A
H (0.0)	58.0	57.5	57.5	57.5	57.5	57.5
H(12.5)	61.5	61.0	61.0	61.0	61.0	61.0
H(25.0)	65.5	65.5	65.5	65.5	65.5	65.5
H(37.5)	68.0	68.0	68.0	68.0	68.0	68.0
H(50.0)	70.0	70.0	70.0	70.0	70.0	70.0
H(62.5)	72.0	71.5	71.5	71.5	71.5	71.5
H(75.0)	81.5	81.0	81.0	81.0	81.0	81.0
H(87.5)	85.5	85.0	85.0	85.0	85.0	85.0
Hs	89.5	89.0	89.0	89.0	89.0	89.0

Table III-9 Hardness Distribution

	Ex. III-17	Ex. III-18	Ex. III-19	Ex. III-20	Ex. III-21
Composition	A	A	A	A	A
H (0.0)	57.5	57.5	57.5	57.5	57.5
H(12.5)	61.0	61.0	61.0	61.0	61.0
H(25.0)	65.5	65.5	65.5	65.5	65.5
H(37.5)	68.0	68.0	68.0	68.0	68.0
H(50.0)	70.0	70.0	70.0	70.0	70.0
H(62.5)	71.5	71.5	71.5	71.5	71.5
H(75.0)	81.0	81.0	81.0	81.0	81.0
H(87.5)	85.0	85.0	85.0	85.0	85.0
Hs	89.0	89.0	89.0	89.0	89.0

EP 3 329 971 B1

Table III-10 Hardness Distribution

	Comp. Ex. III-3	Comp. Ex. III-4	Comp. Ex. III-5	Comp. Ex. III-6	Comp. Ex. III-7	Comp. Ex. III-8	Comp. Ex. III-9
5 Composition	A	A	A	B	A	A	P/Q
H(0)	57.5	57.5	57.5	57.0	57.5	57.5	56.0
H(12.5)	61.0	61.0	61.0	68.0	61.0	61.0	58.0
10 H(25)	65.5	65.5	65.5	73.0	65.5	65.5	59.0
H(37.5)	68.0	68.0	68.0	74.0	68.0	68.0	60.0
H(50)	70.0	70.0	70.0	74.0	70.0	70.0	64.0
H(62.5)	71.5	71.5	71.5	74.0	71.5	71.5	68.0
15 H(75)	81.0	81.0	81.0	78.0	81.0	81.0	79.5
H(87.5)	85.0	85.0	85.0	82.0	85.0	85.0	81.0
Hs	89.0	89.0	89.0	87.0	89.0	89.0	88.0

Table III-11 Results of Evaluation

	Ex. III-1	Comp.Ex. III-1	Ex. III-2	Ex. III-3	Ex. III-4
25 Core Comp.	A	C	D	E	F
Diameter (mm)	39.5	39.5	39.5	39.5	39.5
Hs - H(0)	31.5	31.0	31.5	30.0	27.5
R ²	0.97	0.89	0.96	0.98	0.98
30 Gradient	0.31	0.24	0.28	0.31	0.25
Mid layer					
Composition	M1	M1	M1	M1	M1
Hm	65	65	65	65	65
35 Tm (mm)	1.0	1.0	1.0	1.0	1.0
Inner cover					
Composition	C3	C3	C3	C3	C3
40 Hc1	47	47	47	47	47
T1 (mm)	0.3	0.3	0.3	0.3	0.3
Outer cover					
Composition	C1	C1	C1	C1	C1
45 Hc2	29	29	29	29	29
T2 (mm)	0.3	0.3	0.3	0.3	0.3
Hm - Hc1	18	18	18	18	18
50 Hm - Hc2	36	36	36	36	36
Hc1 - Hc2	18	18	18	18	18
Hs - Hc1	42	41	42	39	36
55 T1 + T2	0.6	0.6	0.6	0.6	0.6
T1 - T2	0.0	0.0	0.0	0.0	0.0
Comp'n (mm)	2.9	2.9	2.8	2.8	2.8

EP 3 329 971 B1

(continued)

Outer cover					
Composition	C1	C1	C1	C1	C1
W#1 spin (rpm)	3150	3270	3100	3000	3100
W#1 flight (m)	239	234	241	243	241
SW spin (rpm)	7100	7150	7000	6950	6950
Durability	115	111	110	107	105

Table III-12 Results of Evaluation

	Comp.Ex. III-2	Ex. III-5	Ex. III-6	Ex. 111-7	Ex. III-8
Core Comp.	G	H	I	J	K
Diameter (mm)	39.9	39.5	39.5	39.5	39.5
Hs - H(0)	13.0	32.5	31.5	32.0	31.5
R ²	0.95	0.98	0.99	0.97	0.98
Gradient	0.11	0.32	0.32	0.32	0.32
Mid layer					
Composition	M1	M1	M1	M1	M1
Hm	65	65	65	65	65
Tm (mm)	1.0	1.0	1.0	1.0	1.0
Inner cover					
Composition	C1	C3	C3	C3	C3
Hc1	29	47	47	47	47
T1 (mm)	0.4	0.3	0.3	0.3	0.3
Outer cover					
Composition	-	C1	C1	C1	C1
Hc2	-	29	29	29	29
T2 (mm)	-	0.3	0.3	0.3	0.3
Hm - Hc1	36	18	18	18	18
Hm - Hc2	-	36	36	36	36
Hc1 - Hc2	-	18	18	18	18
Hs - Hc1	50	42	40	42	41
T1 + T2	0.4	0.6	0.6	0.6	0.6
T1 - T2	-	0.0	0.0	0.0	0.0
Comp'n (mm)	2.8	2.8	2.8	2.8	2.8
W#1 spin (rpm)	3250	3000	2950	3050	3000
W#1 flight (m)	234	243	244	242	243
SW spin (rpm)	7000	7000	6950	7000	6950
Durability	104	109	110	108	109

EP 3 329 971 B1

Table III-13 Results of Evaluation

	Ex. III-9	Ex. III-10	Ex III-11	Ex. III-12	Ex. III-13
Core Comp.	L	M	N	A	A
Diameter (mm)	39.5	39.5	39.5	39.1	39.1
Hs - H(0)	27.0	32.0	31.5	31.5	31.5
R ²	0.96	0.98	0.96	0.97	0.97
Gradient	0.27	0.32	0.31	0.31	0.31
Mid layer					
Composition	M1	M1	M2	M1	M1
Hm	65	65	58	65	65
Tm (mm)	1.0	1.0	1.0	1.0	1.0
Inner cover					
Composition	C3	C3	C3	C3	C3
Hc1	47	47	47	47	47
T1 (mm)	0.3	0.3	0.3	0.4	0.5
Outer cover					
Composition	C1	C1	C1	C1	C1
Hc2	29	29	29	29	29
T2 (mm)	0.3	0.3	0.3	0.4	0.3
Hm - Hc1	18	18	11	18	18
Hm - Hc2	36	36	29	36	36
Hc1 - Hc2	18	18	18	18	18
Hs - Hc1	40	42	43	42	42
T1 + T2	0.6	0.6	0.6	0.8	0.8
T1 - T2	0.0	0.0	0.0	0.0	0.2
Comp'n (mm)	2.8	2.8	2.8	2.9	2.9
W#1 spin (rpm)	3100	3000	3150	3250	3200
W#1 flight (m)	240	243	238	238	239
SW spin (rpm)	7050	7000	7250	7200	7150
Durability	110	108	115	115	115

Table III-14 Results of Evaluation

	Ex. III-14	Ex. III-15	Ex. III-16	Ex. III-17	Ex. III-18
Core Comp.	A	A	A	A	A
Diameter (mm)	39.1	39.5	39.5	39.5	38.3
Hs - H(0)	31.5	31.5	31.5	31.5	31.5
R ²	0.97	0.97	0.97	0.97	0.97
Gradient	0.31	0.31	0.31	0.31	0.31

EP 3 329 971 B1

(continued)

5
10
15
20
25
30
35

Mid layer					
Composition	M1	M1	M1	M1	M1
Hm	65	65	65	65	65
Tm (mm)	1.0	1.0	1.0	1.0	1.0
Inner cover					
Composition	C3	C3	C6	C1	C3
Hc1	47	47	30	29	47
T1 (mm)	0.3	0.3	0.3	0.3	0.6
Outer cover					
Composition	C1	C5	C1	C3	C1
Hc2	29	46	29	47	29
T2 (mm)	0.5	0.3	0.3	0.3	0.6
Hm - Hc1	18	18	35	36	18
Hm - Hc2	36	19	36	18	36
Hc1 - Hc2	18	1	1	-18	18
Hs - Hc1	42	42	59	60	42
T1 + T2	0.8	0.6	0.6	0.6	1.2
T1 - T2	-0.2	0.0	0.0	0.0	0.0
Comp'n (mm)	2.9	2.9	2.9	2.9	2.9
W#1 spin (rpm)	3300	3150	3300	3150	3400
W#1 flight (m)	237	239	237	239	230
SW spin (rpm)	7250	6950	7150	6900	7350
Durability	115	115	115	115	115

Table III-15 Results of Evaluation

40
45
50
55

	Ex. III-19	Ex. III-20	Ex. III-21	Comp.Ex . III-3	Comp.Ex .III-4
Core Comp.	A	A	A	A	A
Diameter (mm)	40.3	39.1	39.1	39.5	39.5
Hs - H(0)	31.5	31.5	31.5	31.5	31.5
R ²	0.97	0.97	0.97	0.97	0.97
Gradient	0.31	0.31	0.31	0.31	0.31
Mid layer					
Composition	M1	M1	M1	M1	M1
Hm	65	65	65	65	65
Tm (mm)	1.0	1.0	1.0	1.0	1.0
Inner cover					
Composition	C3	C3	C3	C1	C2
Hc1	47	47	47	29	36

EP 3 329 971 B1

(continued)

	Inner cover					
5	Composition	C3	C3	C3	C1	C2
	T1 (mm)	0.1	0.65	0.15	0.6	0.6
	Outer cover					
10	Composition	C1	C1	C1	-	-
	Hc2	29	29	29	-	-
	T2 (mm)	0.1	0.15	0.65	-	-
15	Hm - Hc1	18	18	18	36	29
	Hm - Hc2	36	36	36	-	-
	Hc1 - Hc2	18	18	18	-	-
	Hs - Hc1	42	42	42	60	53
20	T1 + T2	0.2	0.8	0.8	0.6	0.6
	T1 - T2	0.0	0.5	-0.5	-	-
	Comp'n (mm)	2.9	2.9	2.9	2.9	2.9
	W#1 spin (rpm)	3000	3150	3400	3300	3200
25	W#1 flight (m)	241	239	236	237	238
	SW spin (rpm)	6700	6800	7400	7150	7000
	Durability	110	115	115	115	115

30

Table III-16 Results of Evaluation

	Comp.Ex .III-5	Comp.Ex .III-6	Comp.Ex .III-7	Comp.Ex .III-8	Comp.Ex .III-9	
35	Core Comp.	A	B	A	A	P/Q
	Diameter (mm)	39.5	39.5	39.3	39.3	39.5
	Hs - H(0)	31.5	30.0	31.5	31.5	32.0
	R ²	0.97	0.86	0.97	0.97	0.97
40	Gradient	0.31	0.23	0.31	0.31	0.31
	Mid layer					
	Composition	M1	M1	M2	M2	M1
45	Hm	65	65	58	58	65
	Tm (mm)	1.0	1.0	1.0	1.0	1.0
	Inner cover					
	Composition	C3	C3	C4	C3	C3
50	Hc1	47	47	60	47	47
	T1 (mm)	0.6	0.3	0.4	0.3	0.3
	Outer cover					
	Composition	-	C1	C1	C4	C1
55	Hc2	-	29	29	60	29
	T2 (mm)	-	0.3	0.3	0.4	0.3

EP 3 329 971 B1

(continued)

	Outer cover					
5	Composition	-	C1	C1	C4	C1
	Hm - Hc1	18	18	-2	11	18
	Hm - Hc2	-	36	29	-2	36
10	Hc1 - Hc2	-	18	31	-13	18
	Hs - Hc1	42	40	29	42	41
	T1 + T2	0.6	0.6	0.7	0.7	0.6
	T1 - T2	-	0.0	0.1	-0.1	0.0
15	Comp'n (mm)	2.9	2.9	2.8	2.9	2.8
	W#1 spin (rpm)	3150	3300	2750	2800	3100
	W#1 flight (m)	239	232	248	245	241
	SW spin (rpm)	6900	7150	6800	6600	7000
20	Durability	115	110	85	90	70

[0361] As shown in Tables III-11 to III-16, the golf balls according to Examples are excellent in various performance characteristics. From the results of evaluation, advantages of the present invention are clear.

[Experiment 4]

[Example IV-1]

[0362] A rubber composition was obtained by kneading 100 parts by weight of a high-cis polybutadiene (trade name "BR-730", manufactured by JSR Corporation), 36 parts by weight of zinc diacrylate (trade name "Sanceler SR", manufactured by SANSHIN CHEMICAL INDUSTRY CO., LTD.), 5 parts by weight of zinc oxide, an appropriate amount of barium sulfate, 0.32 parts by weight of 2-thionaphthol, 0.8 parts by weight of dicumyl peroxide, and 10 parts by weight of zinc stearate. This rubber composition was placed into a mold including upper and lower mold halves each having a hemispherical cavity, and heated at 170°C for 25 minutes to obtain a core with a diameter of 39.5 mm. The amount of barium sulfate was adjusted such that the weight of a golf ball is 45.6 g.

[0363] A resin composition was obtained by kneading 55 parts by weight of an ionomer resin (the aforementioned "Surlyn 8945"), 45 parts by weight of another ionomer resin (the aforementioned "Himilan AM7329"), and 3 parts by weight of titanium dioxide with a twin-screw kneading extruder. The core was placed into a mold. The resin composition was injected around the core by injection molding to form a mid layer with a thickness of 1.0 mm.

[0364] A paint composition (trade name "POLIN 750LE", manufactured by SHINTO PAINT CO., LTD.) including a two-component curing type epoxy resin as a base polymer was prepared. The base material liquid of this paint composition includes 30 parts by weight of a bisphenol A type solid epoxy resin and 70 parts by weight of a solvent. The curing agent liquid of this paint composition includes 40 parts by weight of a modified polyamide amine, 55 parts by weight of a solvent, and 5 parts by weight of titanium dioxide. The weight ratio of the base material liquid to the curing agent liquid is 1/1. This paint composition was applied to the surface of the mid layer with a spray gun, and kept at 23°C for 12 hours to obtain a reinforcing layer with a thickness of 10 μm.

[0365] A resin composition was obtained by kneading 100 parts by weight of a thermoplastic polyurethane elastomer (the aforementioned "Elastollan NY82A"), 0.2 parts by weight of a hindered amine light stabilizer (trade name "TINUVIN 770", manufactured by Ciba Japan K.K.), 4 parts by weight of titanium dioxide, and 0.04 parts by weight of ultramarine blue with a twin-screw kneading extruder. Half shells were formed from this resin composition by compression molding. The sphere consisting of the core, the mid layer, and the reinforcing layer was covered with two of these half shells. The sphere and the half shells were placed into a mold including upper and lower mold halves each having a hemispherical cavity. An inner cover was obtained from the half shells by compression molding. The thickness of the inner cover was 0.3 mm.

[0366] A resin composition was obtained by kneading 100 parts by weight of a thermoplastic polyurethane elastomer (the aforementioned "Elastollan NY97A"), 0.2 parts by weight of a hindered amine light stabilizer (trade name "TINUVIN 770", manufactured by Ciba Japan K.K.), 4 parts by weight of titanium dioxide, and 0.04 parts by weight of ultramarine

EP 3 329 971 B1

blue with a twin-screw kneading extruder. Half shells were formed from this resin composition by compression molding. The sphere consisting of the core, the mid layer, the reinforcing layer, and the inner cover was covered with two of these half shells. The sphere and the half shells were placed into a final mold that includes upper and lower mold halves each having a hemispherical cavity and that has a large number of pimples on its cavity face. An outer cover was obtained from the half shells by compression molding. The thickness of the outer cover was 0.3 mm. Dimples having a shape that is the inverted shape of the pimples were formed on the outer cover. A clear paint including a two-component curing type polyurethane as a base material was applied to this outer cover to obtain a golf ball of Example IV-1 with a diameter of 42.7 mm.

[Examples IV-2 to IV-21 and Comparative Examples IV-1 to IV-9]

[0367] Golf balls of Examples IV-2 to IV-21 and Comparative Examples IV-1 to IV-9 were obtained in the same manner as Example IV-1, except the specifications of the core, the mid layer, the inner cover, and the outer cover were as shown in Tables IV-12 to IV-17 below. The composition of the core is shown in detail in Tables IV-1 to IV-3 below. The composition of the mid layer is shown in detail in Table IV-4 below. The compositions of the inner cover and the outer cover are shown in detail in Table IV-5 below. A hardness distribution of the core is shown in Tables IV-6 to IV-11 below.

[Hit with Driver (W#1)]

[0368] A driver with a titanium head (trade name "XXIO", manufactured by DUNLOP SPORTS CO. LTD., shaft hardness: S, loft angle: 10.0°) was attached to a swing machine manufactured by True Temper Co. A golf ball was hit under the condition of a head speed of 45 m/sec. The spin rate was measured immediately after the hit. Furthermore, the distance from the launch point to the stop point was measured. The average value of data obtained by 10 measurements is shown in Tables IV-12 to IV-17 below.

[Hit with Sand Wedge (SW)]

[0369] A sand wedge (SW) was attached to the above swing machine. A golf ball was hit under the condition of a head speed of 21 m/sec. The backspin rate was measured immediately after the hit. The average value of data obtained by 10 measurements is shown in Tables IV-12 to IV-17 below.

[Durability]

[0370] A golf ball was kept at 23°C for 12 hours. The above driver was attached to the above swing machine. The golf ball was repeatedly hit under the condition of a head speed of 45 m/sec. The number of hits required to break the golf ball was counted. The average value of numbers of hits obtained by 12 measurements is shown as an index in Tables IV-12 to IV-17 below.

Table IV-1 Composition of Core (parts by weight)

	A	B	C	D	E	F
BR-730	100	100	100	100	100	100
Sanceler SR	36.0	35.0	36.0	36.0	37.0	38.0
ZN-DA90S	-	-	-	-	-	-
Zinc oxide	5	5	5	5	5	5
Barium sulfate	*	*	*	*	*	*
2-thionaphthol	0.32	0.32	0.32	0.32	0.32	0.32
Bis(pentabromoph enyl) disulfide	-	-	-	-	-	-
Dicumyl peroxide	0.8	0.8	0.8	0.8	0.8	0.8
Zinc stearate	10.0	-	0.5	2.0	20.0	30.0
Zinc octoate	-	-	-	-	-	-
Zinc myristate	-	-	-	-	-	-

EP 3 329 971 B1

(continued)

	A	B	C	D	E	F
Acid/salt	10.0	0.0	0.5	2.0	20.0	30.0
* Appropriate amount						

Table IV-2 Composition of Core (parts by weight)

	G	H	I	J	K
BR-730	100	100	100	100	100
Sanceler SR	39.0	39.0	40.0	39.0	40.0
ZN-DA90S	-	-	-	-	-
Zinc oxide	5	5	5	5	5
Barium sulfate	*	*	*	*	*
2-thionaphthol	0.32	0.32	0.32	0.32	0.32
Bis(pentabromop henyl) disulfide	-	-	-	-	-
Dicumyl peroxide	0.8	0.8	0.8	0.8	0.8
Zinc stearate	45.0	-	-	-	-
Zinc octoate	-	5.0	10.0	-	-
Zinc myristate	-	-	-	5.0	10.0
Acid/salt	45.0	5.0	10.0	5.0	10.0
* Appropriate amount					

Table IV-3 Composition of Core (parts by weight)

	L	M	N	P	Q
BR-730	100	100	100	100	100
Sanceler SR	39.0	-	37.0	23.0	35.5
ZN-DA90S	-	36.0	-	-	-
Zinc oxide	5	5	5	5	5
Barium sulfate	*	*	*	*	*
2-thionaphthol	-	0.32	0.32	-	-
Bis(pentabromop henyl) disulfide	0.3	-	-	0.5	0.5
Dicumyl peroxide	0.8	0.8	0.8	0.8	0.8
Zinc stearate	10.0	10.0	10.0	-	-
Zinc octoate	-	-	-	-	-
Zinc myristate	-	-	-	-	-
Acid/salt	10.0	10.0	10.0	0.0	0.0
* Appropriate amount					

[0371] The details of the compounds listed in Tables IV-1 to IV-3 are as follows.

BR730: a high-cis polybutadiene manufactured by JSR Corporation (cis-1, 4-bond content: 96% by weight, 1, 2-

EP 3 329 971 B1

vinyl bond content: 1.3% by weight, Mooney viscosity (ML₁₊₄(100°C)) : 55, molecular weight distribution (Mw/Mn): 3)
 Sanceler SR: zinc diacrylate manufactured by SANSHIN CHEMICAL INDUSTRY CO., LTD. (a product coated with 10% by weight of stearic acid)

ZN-DA90S: zinc diacrylate manufactured by Nihon Jyoryu Kogyo Co., Ltd. (a product coated with 10% by weight of zinc stearate)

Zinc oxide: trade name "Ginrei R" manufactured by Toho Zinc Co., Ltd.

Barium sulfate : trade name "Barium Sulfate BD" manufactured by Sakai Chemical Industry Co., Ltd.

2-thionaphthol: a product of Tokyo Chemical Industry Co., Ltd.

Bis(pentabromophenyl)disulfide: a product of Kawaguchi Chemical Industry Co., LTD.

Dicumyl peroxide: trade name "Percumyl D" manufactured by NOF Corporation

Zinc stearate: a product of Wako Pure Chemical Industries, Ltd.

Zinc octoate: a product of Mitsuwa Chemicals Co., Ltd.

Zinc myristate : a product of Wako Pure Chemical Industries, Ltd.

Table IV-4 Composition of Mid Layer (parts by weight)

	M1	M2
Surlyn 8945	55	47
Himilan AM7329	45	45
Rabalon T3221C	-	8
Titanium dioxide	3	3
Hardness (ShoreD)	65	58

Table IV-5 Composition of Cover (parts by weight)

	C1	C2	C3	C4	C5	C6
Elastollan NY82A	100	-	-	-	-	60
Elastollan NY85A	-	50	-	-	-	40
Elastollan NY90A	-	50	-	-	5	-
Elastollan NY97A	-	-	100	-	95	-
Surlyn 8945	-	-	-	40	-	-
Himilan AM7329	-	-	-	55	-	-
Rabalon T3221C	-	-	-	5	-	-
TINUVIN 770	0.2	0.2	0.2	0.2	0.2	0.2
Titanium dioxide	4	4	4	4	4	4
Ultramarine blue	0.04	0.04	0.04	0.04	0.04	0.04
Hardness (Shore D)	29	36	47	60	46	30

Table IV-6 Hardness of Core

	Ex. IV-1	Comp. Ex.IV-1	Comp. Ex.IV-2	Comp. Ex.IV-3	Ex. IV-2
Composition	A	A	A	A	A
H (0.0)	57.5	57.5	57.5	57.5	57.5
H(12.5)	61.0	61.0	61.0	61.0	61.0
H(25.0)	65.5	65.5	65.5	65.5	65.5
H(37.5)	68.0	68.0	68.0	68.0	68.0

EP 3 329 971 B1

(continued)

	Ex. IV-1	Comp. Ex. IV-1	Comp. Ex. IV-2	Comp. Ex. IV-3	Ex. IV-2
H(50.0)	70.0	70.0	70.0	70.0	70.0
H(62.5)	71.5	71.5	71.5	71.5	71.5
H(75.0)	81.0	81.0	81.0	81.0	81.0
H(87.5)	85.0	85.0	85.0	85.0	85.0
Hs	89.0	89.0	89.0	89.0	89.0
Hs - H(0.0)	31.5	31.5	31.5	31.5	31.5
R ²	0.97	0.97	0.97	0.97	0.97
Diameter (mm)	39.5	39.5	39.5	39.5	39.5

Table IV-7 Hardness of Core

	Ex. IV-3	Comp. Ex. IV-4	Comp. Ex. IV-5	Comp. Ex. IV-6	Comp. Ex. IV-7	Comp. Ex. IV-8
Composition	A	B	C	A	A	A
H(0.0)	57.5	57.0	57.0	57.5	57.5	57.5
H(12.5)	61.0	68.0	67.5	61.0	61.0	61.0
H(25.0)	65.5	73.0	72.0	65.5	65.5	65.5
H(37.5)	68.0	74.0	73.0	68.0	68.0	68.0
H(50.0)	70.0	74.0	74.0	70.0	70.0	70.0
H(62.5)	71.5	74.0	74.5	71.5	71.5	71.5
H(75.0)	81.0	78.0	78.0	81.0	81.0	81.0
H(87.5)	85.0	82.0	82.5	85.0	85.0	85.0
Hs	89.0	87.0	88.0	89.0	89.0	89.0
Hs - H(0.0)	31.5	30.0	31.0	31.5	31.5	31.5
R ²	0.97	0.86	0.89	0.97	0.97	0.97
Diameter (mm)	39.5	38.9	38.9	38.9	38.3	40.3

Table IV-8 Hardness of Core

	Ex. IV-4	Ex. IV-5	Ex. IV-6	Ex. IV-7	Ex. IV-8	Ex. IV-9
Composition	A	A	D	E	F	G
H(0.0)	57.5	57.5	57.0	56.0	55.5	66.0
H(12.5)	61.0	61.0	62.5	59.0	60.5	69.0
H(25.0)	65.5	65.5	69.0	62.0	63.0	71.0
H(37.5)	68.0	68.0	70.5	65.5	66.0	72.0
H(50.0)	70.0	70.0	72.0	69.0	68.5	72.0
H(62.5)	71.5	71.5	73.0	71.0	70.0	73.0
H(75.0)	81.0	81.0	79.5	80.0	74.5	74.5
H(87.5)	85.0	85.0	83.5	82.0	77.0	77.0
Hs	89.0	89.0	88.5	86.0	83.0	79.0

EP 3 329 971 B1

(continued)

	Ex. IV-4	Ex. IV-5	Ex. IV-6	Ex. IV-7	Ex. IV-8	Ex. IV-9
Hs - H(0.0)	31.5	31.5	31.5	30.0	27.5	13.0
R ²	0.97	0.97	0.96	0.98	0.98	0.95
Diameter (mm)	38.3	40.3	38.9	38.9	38.9	39.5

Table IV-9 Hardness of Core

	Ex. IV-10	Ex. IV-11	Ex. IV-12	Ex. IV-13	Ex. IV-14
Composition	H	I	J	K	L
H (0.0)	56.5	55.5	57.0	56.0	60.0
H(12.5)	59.5	59.0	60.5	59.5	62.5
H(25.0)	64.5	64.0	65.0	64.5	64.5
H(37.5)	67.0	67.0	68.0	67.5	67.5
H(50.0)	70.0	69.5	70.0	69.5	70.0
H(62.5)	72.0	72.0	72.0	72.0	71.5
H(75.0)	80.5	80.0	80.5	80.5	80.0
H(87.5)	85.0	84.0	85.0	84.5	83.0
Hs	89.0	87.0	89.0	87.5	87.0
Hs - H(0.0)	32.5	31.5	32.0	31.5	27.0
R ²	0.98	0.99	0.97	0.98	0.96
Diameter (mm)	38.9	38.9	38.9	38.9	38.9

Table IV-10 Hardness of Core

	Ex. IV-15	Ex. IV-16	Comp. Ex. IV-9	Ex. IV-17
Composition	M	N	A	A
H (0.0)	57.0	58.0	57.5	57.5
H(12.5)	61.0	61.5	61.0	61.0
H(25.0)	65.0	65.5	65.5	65.5
H(37.5)	67.5	68.0	68.0	68.0
H(50.0)	70.0	70.0	70.0	70.0
H(62.5)	73.0	72.0	71.5	71.5
H(75.0)	80.5	81.5	81.0	81.0
H(87.5)	85.0	85.5	85.0	85.0
Hs	89.0	89.5	89.0	89.0
Hs - H(0.0)	32.0	31.5	31.5	31.5
R ²	0.98	0.96	0.97	0.97
Diameter (mm)	38.9	38.9	39.3	38.9

EP 3 329 971 B1

Table IV-11 Hardness of Core

	Ex. IV-18	Ex. IV-19	Ex. IV-20	Ex. IV-21
Composition	A	A	A	A
H (0.0)	57.5	57.5	57.5	57.5
H(12.5)	61.0	61.0	61.0	61.0
H(25.0)	65.5	65.5	65.5	65.5
H(37.5)	68.0	68.0	68.0	68.0
H(50.0)	70.0	70.0	70.0	70.0
H(62.5)	71.5	71.5	71.5	71.5
H(75.0)	81.0	81.0	81.0	81.0
H(87.5)	85.0	85.0	85.0	85.0
Hs	89.0	89.0	89.0	89.0
Hs - H(0.0)	31.5	31.5	31.5	31.5
R ²	0.97	0.97	0.97	0.97
Diameter (mm)	39.1	39.1	39.1	39.1

Table IV-12 Results of Evaluation

	Ex. IV-1	Comp. Ex.IV-1	Comp. Ex.IV-2	Comp. Ex.IV-3	Ex. IV-2
Core					
Composition	A	A	A	A	A
Acid or salt (PHR)	10.0	10.0	10.0	10.0	10.0
Mid layer					
Composition	M1	M1	M1	M1	M1
Hm (Shore D)	65	65	65	65	65
Thickness Tm (mm)	1.0	1.0	1.0	1.0	1.0
Inner cover					
Composition	C1	C1	C2	C3	C5
Hc1 (Shore D)	29	29	36	47	46
Thickness Tc1 (mm)	0.3	0.3	0.3	0.3	0.3
Outer cover					
Composition	C3	C1	C2	C3	C3
Hc2 (Shore D)	47	29	36	47	47
Thickness Tc2 (mm)	0.3	0.3	0.3	0.3	0.3
Hm - Hc1	36	36	29	18	19
Hm - Hc2	18	36	29	18	18
Hc2 - Hc1	18	0	0	0	1
Tc1 + Tc2 (mm)	0.6	0.3	0.6	0.6	0.6
Tc2 - Tc1 (mm)	0	0	0	0	0
Ball Comp'n (mm)	2.9	2.9	2.9	2.9	2.9
W#1 spin (rpm)	3150	3300	3200	3150	3150

EP 3 329 971 B1

(continued)

Outer cover					
Composition	C3	C1	C2	C3	C3
W#1 flight (m)	239	237	238	239	239
SW spin (rpm)	7100	7150	7000	6900	6950
Durability	115	115	115	115	115

Table IV-13 Results of Evaluation

	Ex. IV-3	Comp. Ex. IV-4	Comp. Ex. IV-5	Comp. Ex. IV-6	Comp. Ex. IV-7	Comp. Ex. IV-8
Core						
Composition	A	B	C	A	A	A
Acid or salt (PHR)	10.0	0.0	0.5	10.0	10.0	10.0
Mid layer						
Composition	M1	M1	M1	M1	M1	M1
Hm (Shore D)	65	65	65	65	65	65
Thickness Tm (mm)	1.0	1.0	1.0	1.0	1.0	1
Inner cover						
Composition	C1	C1	C1	C3	C3	C3
Hc1 (Shore D)	29	29	29	47	47	47
Thickness Tc1 (mm)	0.3	0.3	0.3	0.6	1.2	0.2
Outer cover						
Composition	C6	C3	C3	C1	-	-
Hc2 (Shore D)	30	47	47	29	-	-
Thickness Tc2 (mm)	0.3	0.6	0.6	0.3	-	-
Hm - Hc1	36	36	36	18	18	18
Hm - Hc2	35	18	18	36	-	-
Hc2 - Hc1	1	18	18	-18	-	-
Tc1 + Tc2 (mm)	0.6	0.9	0.9	0.9	1.2	0.2
Tc2 - Tc1 (mm)	0	0.3	0.3	-0.3	-	-
Ball Comp'n (mm)	2.9	2.9	2.9	2.9	2.9	2.9
W#1 spin (rpm)	3300	3300	3200	3400	3400	3000
W#1 flight (m)	237	232	238	236	235	242
SW spin (rpm)	7250	7150	7150	7300	7400	6800
Durability	115	110	111	115	120	105

EP 3 329 971 B1

Table IV-14 Results of Evaluation

	Ex. IV-4	Ex. IV-5	Ex. IV-6	Ex. IV-7	Ex. IV-8	Ex. IV-9
Core						
Composition	A	A	D	E	F	G
Acid or salt (PHR)	10.0	10.0	2.0	20.0	30.0	45.0
Mid layer						
Composition	M1	M1	M1	M1	M1	M1
Hm (Shore D)	65	65	65	65	65	65
Thickness Tm (mm)	1.0	1.0	1.0	1.0	1.0	1.0
Inner cover						
Composition	C1	C1	C1	C1	C1	C1
Hc1 (Shore D)	29	29	29	29	29	29
Thickness Tc1 (mm)	0.6	0.1	0.3	0.3	0.3	0.3
Outer cover						
Composition	C3	C3	C3	C3	C3	C3
Hc2 (Shore D)	47	47	47	47	47	47
Thickness Tc2 (mm)	0.6	0.1	0.6	0.6	0.6	0.3
Hm - Hc1	36	36	36	36	36	36
Hm - Hc2	18	18	18	18	18	18
Hc2 - Hc1	18	18	18	18	18	18
Tc1 + Tc2 (mm)	1.2	0.2	0.9	0.9	0.9	0.6
Tc2 - Tc1 (mm)	0	0	0.3	0.3	0.3	0
Ball Comp'n (mm)	2.9	2.9	2.8	2.8	2.8	2.8
W#1 spin (rpm)	3400	3000	3100	3000	3100	3200
W#1 flight (m)	235	242	241	243	241	238
SW spin (rpm)	7500	7000	7000	6950	6950	7150
Durability	120	105	110	107	105	104

Table IV-15 Results of Evaluation

	Ex. IV-10	Ex. IV-11	Ex. IV-12	Ex. IV-13	Ex. IV-14
Core					
Composition	H	I	J	K	L
Acid or salt (PHR)	5.0	10.0	5.0	10.0	10.0
Mid layer					
Composition	M1	M1	M1	M1	M1
Hm (Shore D)	65	65	65	65	65
Thickness Tm (mm)	1.0	1.0	1.0	1.0	1.0

EP 3 329 971 B1

(continued)

5

10

15

20

25

Inner cover					
Composition	C1	C1	C1	C1	C1
Hc1 (Shore D)	29	29	29	29	29
Thickness Tc1 (mm)	0.3	0.3	0.3	0.3	0.3
Outer cover					
Composition	C3	C3	C3	C3	C3
Hc2 (Shore D)	47	47	47	47	47
Thickness Tc2 (mm)	0.6	0.6	0.6	0.6	0.6
Hm - Hc1	36	36	36	36	36
Hm - Hc2	18	18	18	18	18
Hc2 - Hc1	18	18	18	18	18
Tc1 + Tc2 (mm)	0.9	0.9	0.9	0.9	0.9
Tc2 - Tc1 (mm)	0.3	0.3	0.3	0.3	0.3
Ball Comp'n (mm)	2.8	2.8	2.8	2.8	2.8
W#1 spin (rpm)	3000	2950	3050	3000	3100
W#1 flight (m)	243	244	242	243	240
SW spin (rpm)	7000	6950	7000	6950	7050
Durability	109	110	108	109	110

30

Table IV-16 Results of Evaluation

35

40

45

50

55

	Ex. IV-15	Ex. IV-16	Comp. Ex.IV-9	Ex. IV-17
Core				
Composition	M	N	A	A
Acid or salt (PHR)	10.0	10.0	10.0	10.0
Mid layer				
Composition	M1	M2	M2	M1
Hm (Shore D)	65	58	58	65
Thickness Tm (mm)	1.0	1.0	1.0	1.0
Inner cover				
Composition	C1	C1	C4	C1
Hc1 (Shore D)	29	29	60	29
Thickness Tc1 (mm)	0.3	0.3	0.3	0.3
Outer cover				
Composition	C3	C3	C1	C3
Hc2 (Shore D)	47	47	29	47
Thickness Tc2 (mm)	0.6	0.6	0.4	0.6
Hm - Hc1	36	29	-2	36
Hm - Hc2	18	11	29	18

EP 3 329 971 B1

(continued)

5

10

15

Outer cover				
Composition	C3	C3	C1	C3
Hc2 - Hc1	18	18	-31	18
Tc1 + Tc2 (mm)	0.9	0.9	0.7	0.9
Tc2 - Tc1 (mm)	0.3	0.3	0.1	0.3
Ball Comp'n (mm)	2.8	2.8	2.8	2.9
W#1 spin (rpm)	3000	3150	3150	3250
W#1 flight (m)	243	238	238	238
SW spin (rpm)	7000	7250	7000	7200
Durability	108	115	130	115

20

25

30

35

40

45

50

55

Table IV-17 Results of Evaluation

	Ex. IV-18	Ex. IV-19	Ex. IV-20	Ex. IV-21
Core				
Composition	A	A	A	A
Acid or salt (PHR)	10.0	10.0	10.0	10.0
Mid layer				
Composition	M1	M1	M1	M1
Hm (Shore D)	65	65	65	65
Thickness Tm (mm)	1.0	1.0	1.0	1.0
Inner cover				
Composition	C1	C1	C1	C1
Hc1 (Shore D)	29	29	29	29
Thickness Tc1 (mm)	0.5	0.3	0.65	0.15
Outer cover				
Composition	C3	C3	C3	C3
Hc2 (Shore D)	47	47	47	47
Thickness Tc2 (mm)	0.3	0.5	0.15	0.65
Hm - Hc1	36	36	36	36
Hm - Hc2	18	18	18	18
Hc2 - Hc1	18	18	18	18
Tc1 + Tc2 (mm)	0.8	0.8	0.8	0.8
Tc2 - Tc1 (mm)	-0.2	0.2	-0.5	0.5
Ball Comp'n (mm)	2.9	2.9	2.9	2.9
W#1 spin (rpm)	3200	3300	3300	3150
W#1 flight (m)	239	237	237	239
SW spin (rpm)	7150	7250	7400	7150
Durability	115	115	115	115

[0372] As shown in Tables IV-12 to IV-17, the golf balls according to Examples are excellent in various performance characteristics. From the results of evaluation, advantages of the present invention are clear.

[0373] The golf ball according to the present invention can be used for playing golf on golf courses and practicing at driving ranges. The above descriptions are merely for illustrative examples, and various modifications can be made without departing from the principles of the present invention as defined by the appended claims.

Claims

- 10 1. A golf ball comprising a core (204), a mid layer (206) positioned outside the core (204), an inner cover (210) positioned outside the mid layer (206), and an outer cover (212) positioned outside the inner cover (210), wherein the core (204) has a diameter of equal to or greater than 38.0 mm, when distances (%) from a central point of the core (204) to nine points and JIS-C hardnesses at the nine points, which nine points are obtained by dividing a region from the central point of the core (204) to a surface of the core (204) at intervals of 12.5% of a radius of the core (204), are plotted in a graph, R^2 of a linear approximation curve obtained by a least-square method is equal to or greater than 0.95, a Shore D hardness H_m of the mid layer (206) is greater than a Shore D hardness H_{c1} of the inner cover (210), wherein either
- 15
- 20 i) the hardness H_m is greater than a Shore D hardness H_{c2} of the outer cover (212), and a thickness T_1 of the inner cover (210) is equal to or greater than 0.1 mm but equal to or less than 0.8 mm, or ii) a Shore D hardness H_{c2} of the outer cover (312) is greater than the hardness H_{c1} .
- 25 2. The golf ball according to claim 1, wherein for alternative i) a difference ($H_m - H_{c1}$) between the hardness H_m and the hardness H_{c1} is equal to or greater than 15.
- 30 3. The golf ball according to claim 1, wherein for alternative i) a difference ($H_m - H_{c2}$) between the hardness H_m and the hardness H_{c2} is equal to or greater than 20.
- 35 4. The golf ball according to claim 1, wherein for alternative i) the core (204) is formed by a rubber composition being crosslinked, the rubber composition includes:
- (a) a base rubber;
- (b) a co-crosslinking agent;
- (c) a crosslinking initiator; and
- (d) an acid and/or a salt, wherein the acid and/or salt excludes the co-crosslinking agent, and
- the co-crosslinking agent (b) is:
- 40 (b1) an α , β -unsaturated carboxylic acid having 3 to 8 carbon atoms; and/or (b2) a metal salt of an α , β -unsaturated carboxylic acid having 3 to 8 carbon atoms.
- 45 5. The golf ball according to claim 1, wherein for alternative ii) a difference ($H_m - H_{c1}$) between the hardness H_m and the hardness H_{c1} is equal to or greater than 20.
6. The golf ball according to claim 1, wherein for alternative ii) the difference ($H_{c2} - H_{c1}$) between the hardness H_{c2} and the hardness H_{c1} is equal to or greater than 5.
- 50 7. The golf ball according to claim 1, wherein for alternative ii) the core (304) is formed by a rubber composition being crosslinked, the rubber composition includes:
- (a) a base rubber;
- 55 (b) a co-crosslinking agent;
- (c) a crosslinking initiator; and
- (d) an acid and/or a salt, wherein the acid and/or salt excludes the co-crosslinking agent, and

the co-crosslinking agent (b) is:

- (b1) an α,β -unsaturated carboxylic acid having 3 to 8 carbon atoms; and/or
 (b2) a metal salt of an α,β -unsaturated carboxylic acid having 3 to 8 carbon atoms.

5

Patentansprüche

10

1. Golfball, umfassend einen Kern (204), eine außerhalb des Kerns (204) angeordnete Mittelschicht (206), eine außerhalb der Mittelschicht (206) angeordnete innere Abdeckung (210) und eine außerhalb der inneren Abdeckung (210) angeordnete äußere Abdeckung (212), wobei

15

der Kern (204) einen Durchmesser von gleich oder größer als 38,0 mm aufweist, wenn Entfernungen (%) von einem Mittelpunkt des Kerns (204) zu neun Punkten und JIS-C-Härten an den neun Punkten, welche neun Punkte durch Teilen eines Bereichs vom Mittelpunkt des Kerns (204) zu einer Oberfläche des Kerns (204) in Intervallen von 12,5% eines Radius des Kerns (204) erhalten werden, in einem Diagramm aufgetragen werden, R^2 einer linearen Näherungskurve, die durch eine Methode der kleinsten Quadrate erhalten wird, gleich oder größer als 0,95 ist, eine Shore D-Härte Hm der Mittelschicht (206) größer als eine Shore D-Härte Hc1 der inneren Abdeckung (210) ist, wobei entweder

20

25

- i) die Härte Hm größer als eine Shore D-Härte Hc2 der äußeren Abdeckung (212) ist, und eine Dicke T1 der Abdeckung (210) gleich oder größer als 0,1 mm, aber gleich oder kleiner als 0,8 mm ist, oder
 ii) eine Shore D-Härte Hc2 der äußeren Abdeckung (312) größer als die Härte Hc1 ist.

30

2. Golfball nach Anspruch 1, wobei für Alternative i) eine Differenz (Hm-Hc1) zwischen der Härte Hm und der Härte Hc1 gleich oder größer als 15 ist.

35

3. Golfball nach Anspruch 1, wobei für Alternative i) eine Differenz (Hm-Hc2) zwischen der Härte Hm und der Härte Hc2 gleich oder größer als 20 ist.

4. Golfball nach Anspruch 1, wobei für Alternative i) der Kern (204) durch eine vernetzte Kautschukzusammensetzung gebildet ist,

wobei die Kautschukzusammensetzung umfasst:

40

- (a) einen Basiskautschuk;
 (b) ein Co-Vernetzungsmittel;
 (c) einen Vernetzungsinitiator; und
 (d) eine Säure und/oder ein Salz, wobei die Säure und/oder das Salz (d) das Co-Vernetzungsmittel (b) ausschließt, und

45

das Co-Vernetzungsmittel (b) ist:

- (b1) eine α,β -ungesättigte Carbonsäure mit 3 bis 8 Kohlenstoffatomen; und/oder
 (b2) ein Metallsalz einer α,β -ungesättigten Carbonsäure mit 3 bis 8 Kohlenstoffatomen.

50

5. Golfball nach Anspruch 1, wobei für Alternative ii) eine Differenz (Hm-Hc1) zwischen der Härte Hm und der Härte Hc1 gleich oder größer als 20 ist.

55

6. Golfball nach Anspruch 1, wobei für Alternative ii) die Differenz (Hc2-Hc1) zwischen der Härte Hc2 und der Härte Hc1 gleich oder größer als 5 ist.

7. Golfball nach Anspruch 1, wobei für die Alternative ii) der Kern (304) durch eine vernetzte Kautschukzusammensetzung gebildet ist,

wobei die Kautschukzusammensetzung umfasst:

- (a) einen Basiskautschuk;
- (b) ein Co-Vernetzungsmittel;
- (c) einen Vernetzungsinitiator; und
- (d) eine Säure und/oder ein Salz, wobei die Säure und/oder das Salz (d) das Co-Vernetzungsmittel (b) ausschließt, und

das Co-Vernetzungsmittel (b) ist:

- (b1) eine α,β -ungesättigte Carbonsäure mit 3 bis 8 Kohlenstoffatomen; und/oder
- (b2) ein Metallsalz einer α,β -ungesättigten Carbonsäure mit 3 bis 8 Kohlenstoffatomen.

Revendications

1. Balle de golf comprenant un cœur (204), une couche moyenne (206) positionnée à l'extérieur du cœur (204), un couvercle interne (210) positionné à l'extérieur de la couche moyenne (206), et un couvercle externe (212) positionné à l'extérieur du couvercle interne (210), dans laquelle le cœur (204) a un diamètre supérieur ou égal à 38,0 mm, lorsque les distances (%) d'un point central du cœur (204) à neuf points et les duretés JIS-C aux neuf points, lesquels neuf points sont obtenus en divisant une région du point central du cœur (204) à une surface du cœur (204) à des intervalles de 12,5 % d'un rayon du cœur (204), sont portés sur un graphe, R^2 d'une courbe d'approximation linéaire obtenue par une méthode des moindres carrés est supérieur ou égal à 0,95, une dureté D Shore Hm de la couche moyenne (206) est supérieure à une dureté D Shore Hc1 du couvercle interne (210), dans laquelle ou

- i) la dureté Hm est supérieure à une dureté D Shore Hc2 du couvercle externe (212), et une épaisseur T1 du couvercle interne (210) est supérieure ou égale à 0,1 mm mais inférieure ou égale à 0,8 mm, ou
- ii) une dureté D Shore Hc2 du couvercle externe (312) est supérieure à la dureté Hc1.

2. Balle de golf selon la revendication 1, dans laquelle pour l'alternative i), une différence (Hm-Hc1) entre la dureté Hm et la dureté Hc1 est supérieure ou égale à 15.

3. Balle de golf selon la revendication 1, dans laquelle pour l'alternative i) une différence (Hm-Hc2) entre la dureté Hm et la dureté Hc2 est supérieure ou égale à 20.

4. Balle de golf selon la revendication 1, dans laquelle pour l'alternative i) le cœur (204) est formé d'une composition de caoutchouc qui est réticulé, la composition de caoutchouc comporte :

- (a) un caoutchouc de base ;
- (b) un agent de co-réticulation ;
- (c) un initiateur de réticulation ; et
- (d) un acide et/ou un sel, dans laquelle l'acide et/ou le sel excluent l'agent de co-réticulation, et

l'agent de co-réticulation (b) est :

- (b1) un acide carboxylique α,β -insaturé ayant 3 à 8 atomes de carbone ; et/ou
- (b2) un sel métallique d'un acide carboxylique α,β -insaturé ayant 3 à 8 atomes de carbone.

5. Balle de golf selon la revendication 1, dans laquelle pour l'alternative ii) une différence (Hm-Hc1) entre la dureté Hm et la dureté Hc1 est supérieure ou égale à 20.

6. Balle de golf selon la revendication 1, dans laquelle pour l'alternative ii) la différence (Hc2-Hc1) entre la dureté Hc2 et la dureté Hc1 est supérieure ou égale à 5.

EP 3 329 971 B1

7. Balle de golf selon la revendication 1, dans laquelle pour l'alternative ii) le cœur (304) est formé par une composition de caoutchouc qui est réticulé, la composition de caoutchouc comporte :

- 5
- (a) un caoutchouc de base ;
 - (b) un agent de co-réticulation ;
 - (c) un initiateur de réticulation ; et
 - (d) un acide et/ou un sel, dans laquelle l'acide et/ou le sel excluent l'agent de co-réticulation, et

10 l'agent de co-réticulation (b) est :

- (b1) un acide carboxylique α,β -insaturé ayant 3 à 8 atomes de carbone ; et/ou
- (b2) un sel métallique d'un acide carboxylique α,β -insaturé ayant 3 à 8 atomes de carbone.

15

20

25

30

35

40

45

50

55

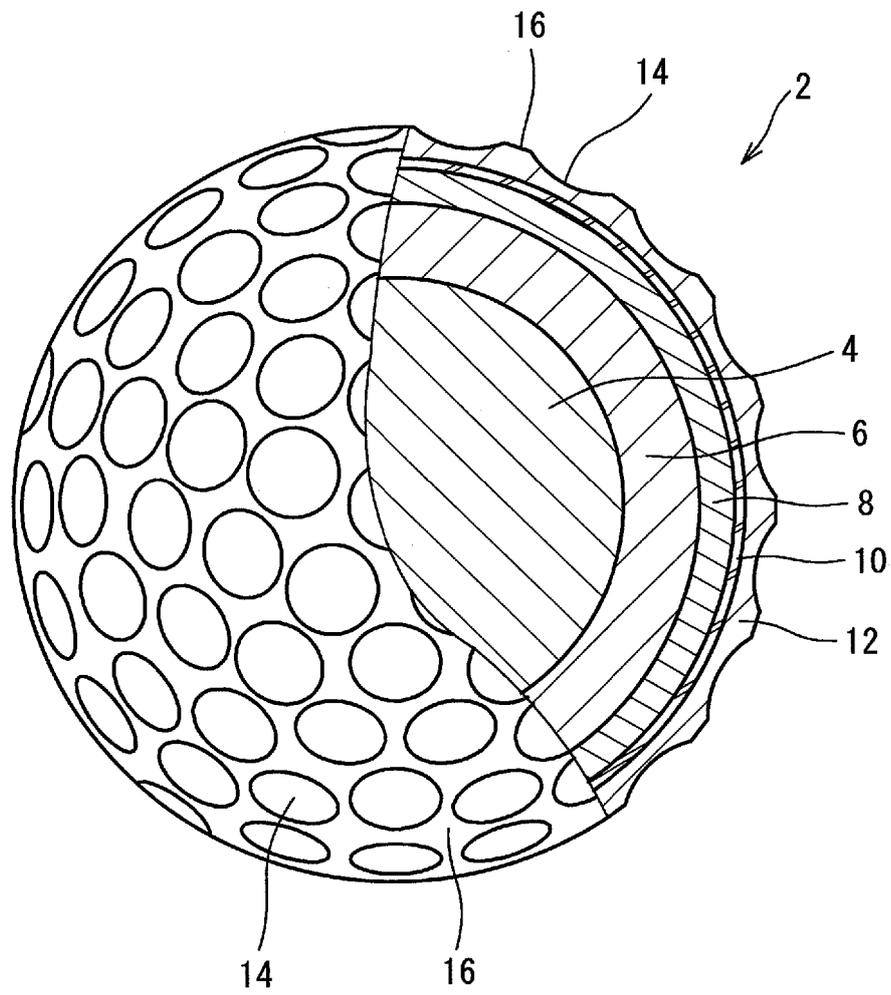


FIG. 1

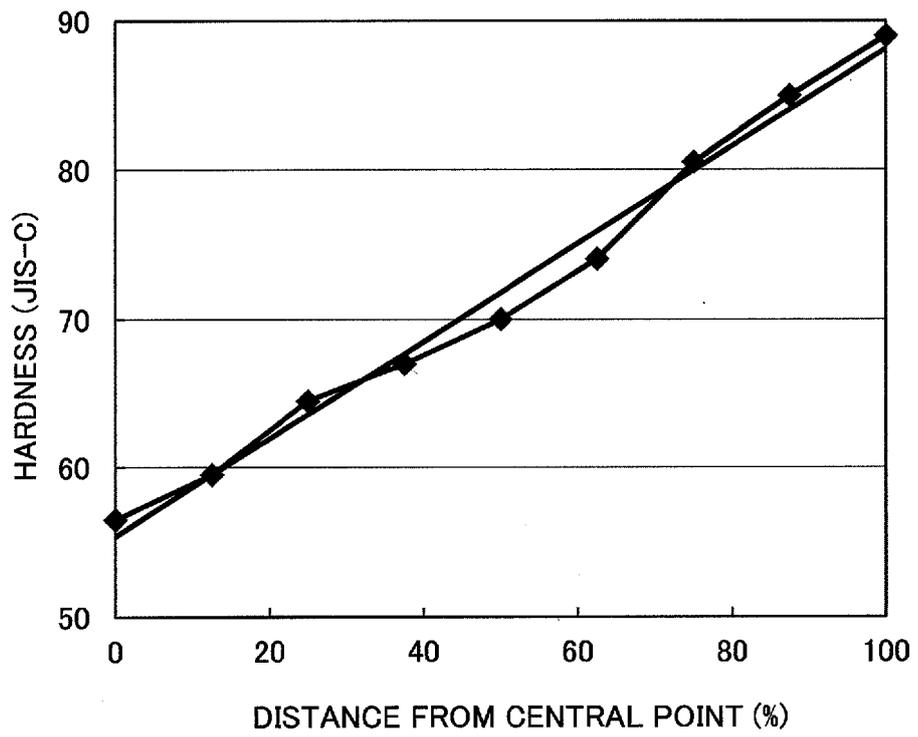


FIG. 2

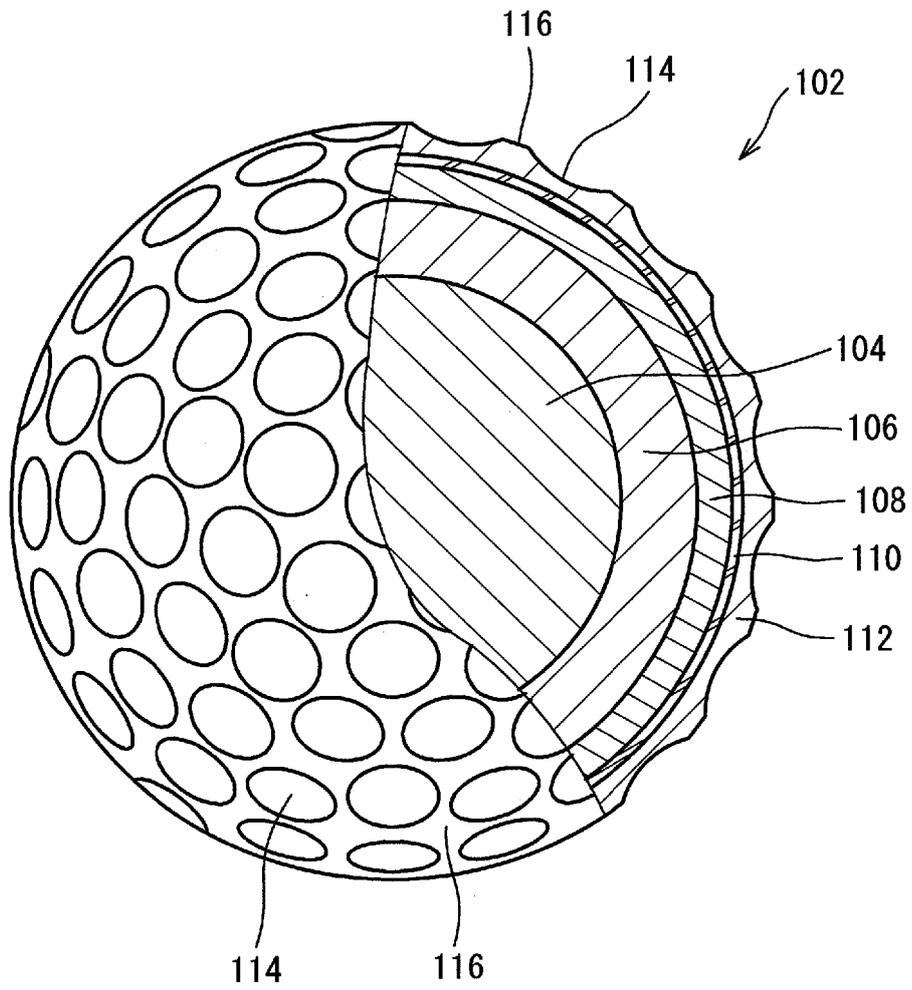


FIG. 3

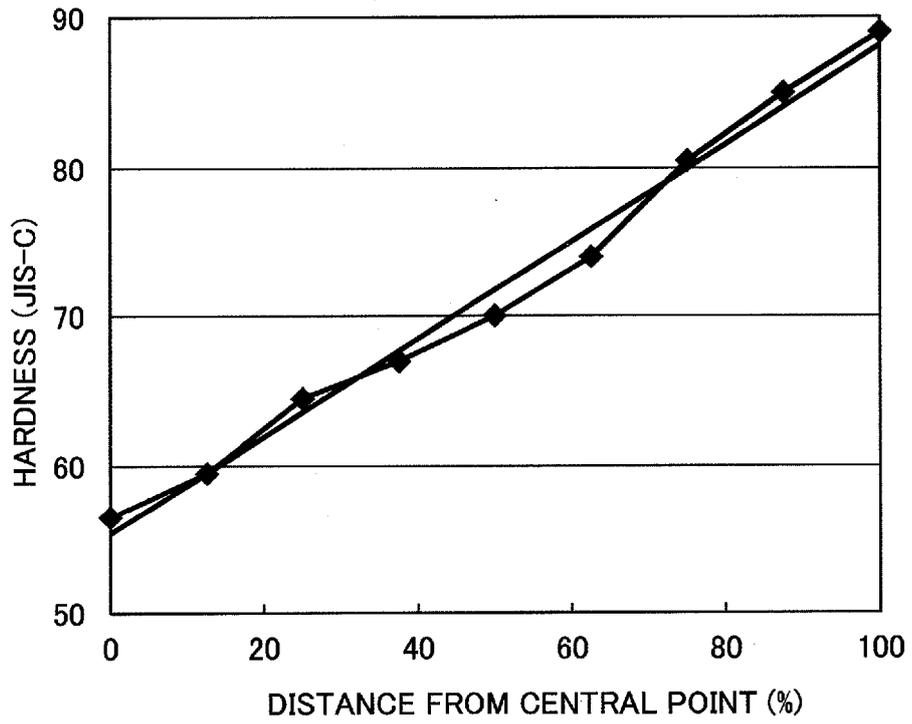


FIG. 4

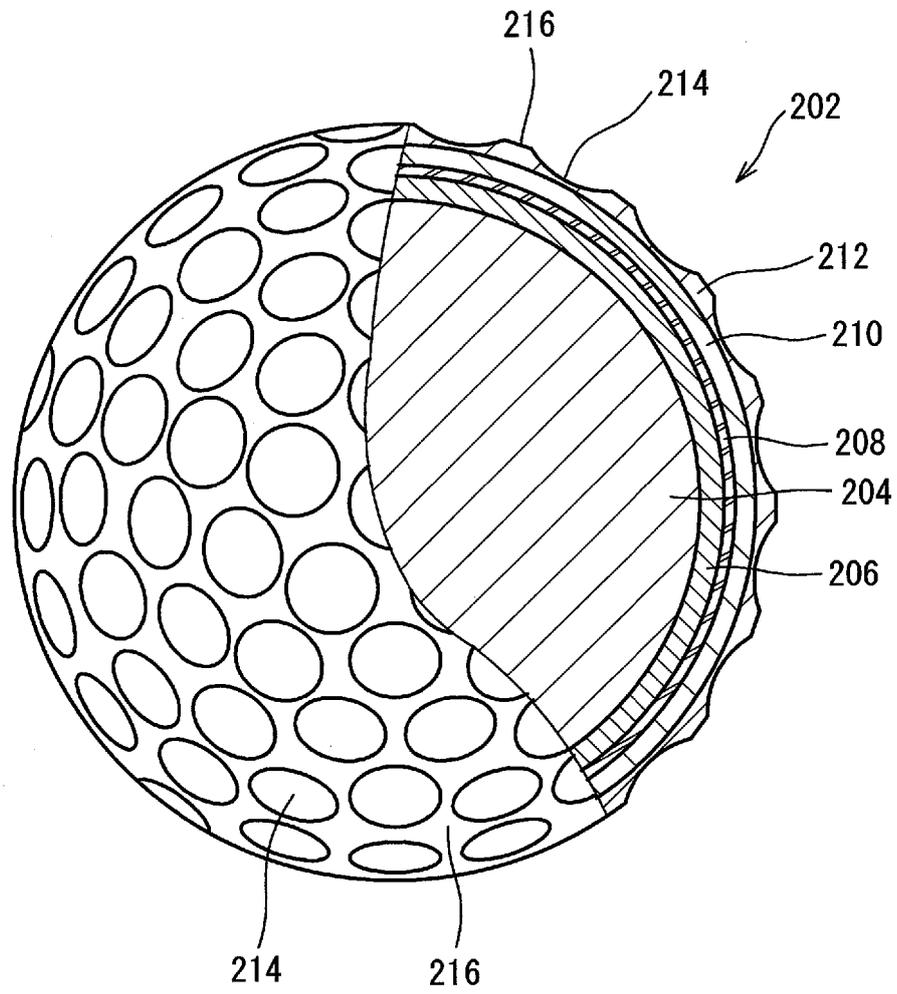


FIG. 5

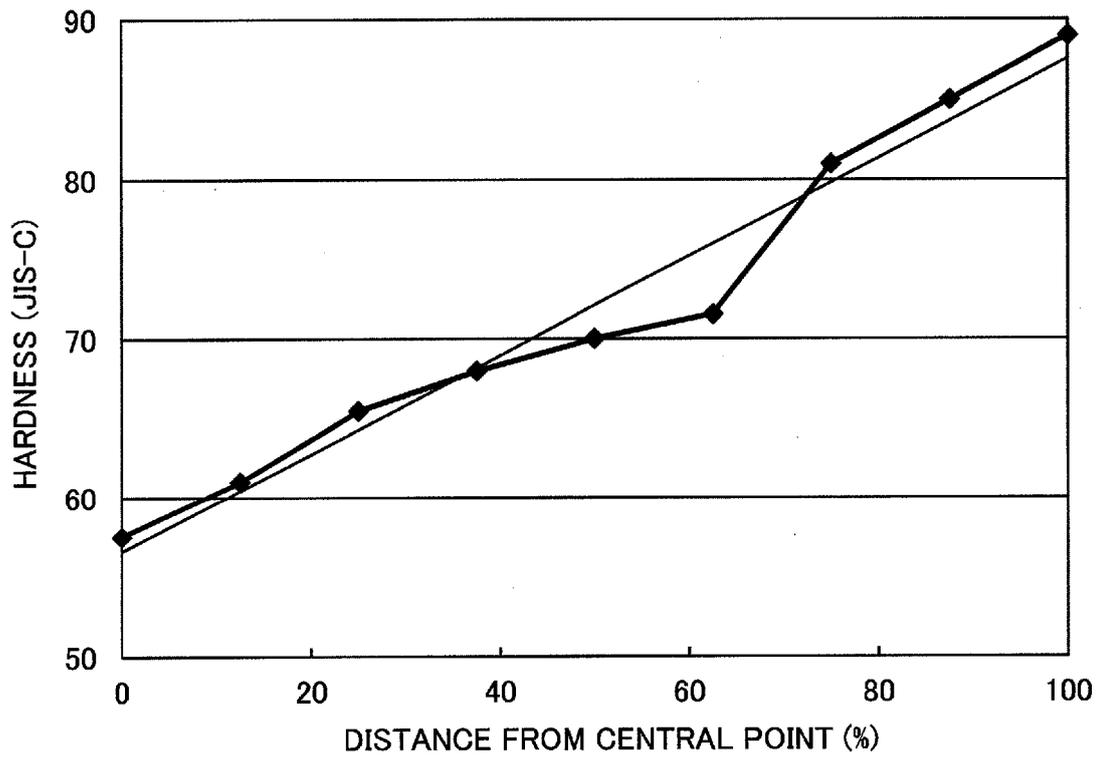


FIG. 6

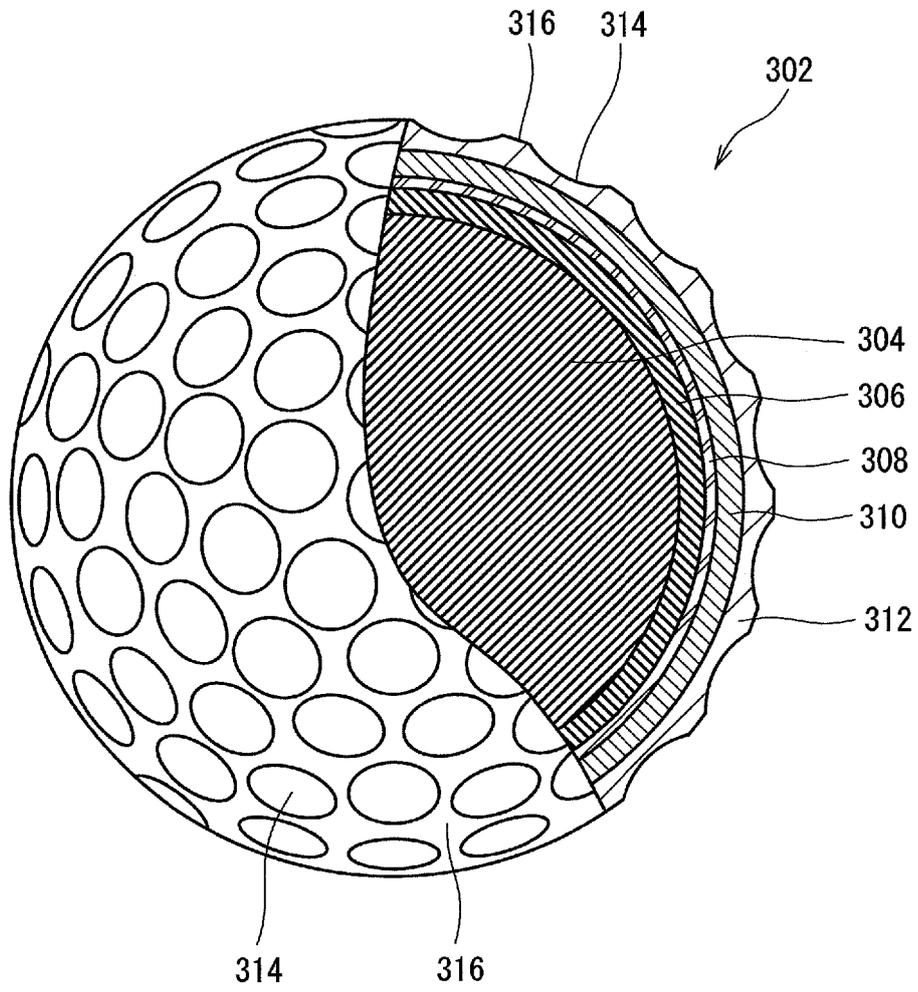


FIG. 7

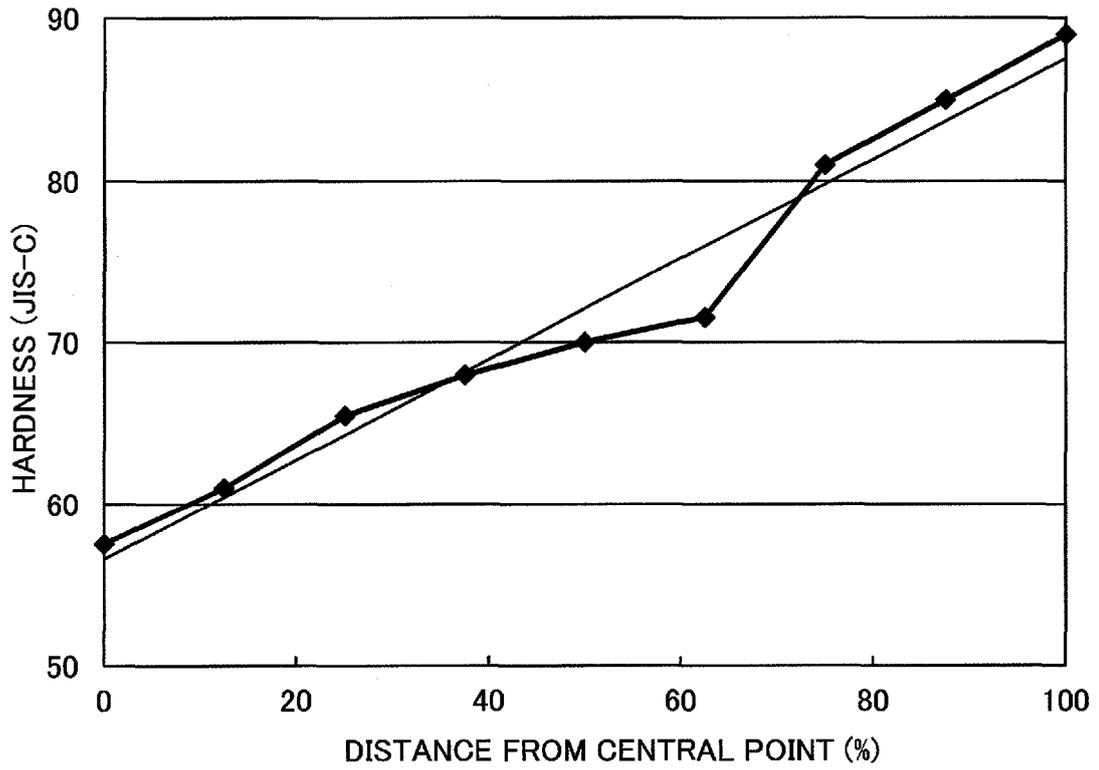


FIG. 8

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2012099641 A [0001]
- JP 2012116542 A [0001]
- JP 2012118422 A [0001]
- JP 2012118544 A [0001]
- JP 2012124924 A [0001]
- JP 2012124249 A [0001]
- JP 61037178 A [0003] [0004]
- JP 2008212681 A [0003] [0005]
- US 20080214324 A [0003]
- JP 2008523952 A [0003] [0006]
- US 20060135287 A [0003]
- US 20070173607 A [0003]
- JP 2009119256 A [0003] [0007]
- US 20090124757 A [0003]
- JP 6154357 A [0008] [0009]
- US P5403010 A [0008]
- JP 2008194471 A [0008] [0010]
- US P7344455 B [0008]
- US 20080194358 A [0008]
- US 20080194359 A [0008]
- US 20080214325 A [0008]
- JP 2008194473 A [0008] [0011]
- US 20080194357 A [0008]
- US 20080312008 A [0008]
- JP 2010253268 A [0012]
- US 20100273575 A [0012]
- US 7850548 B2 [0015]
- US 2008145377 A1 [0015]