



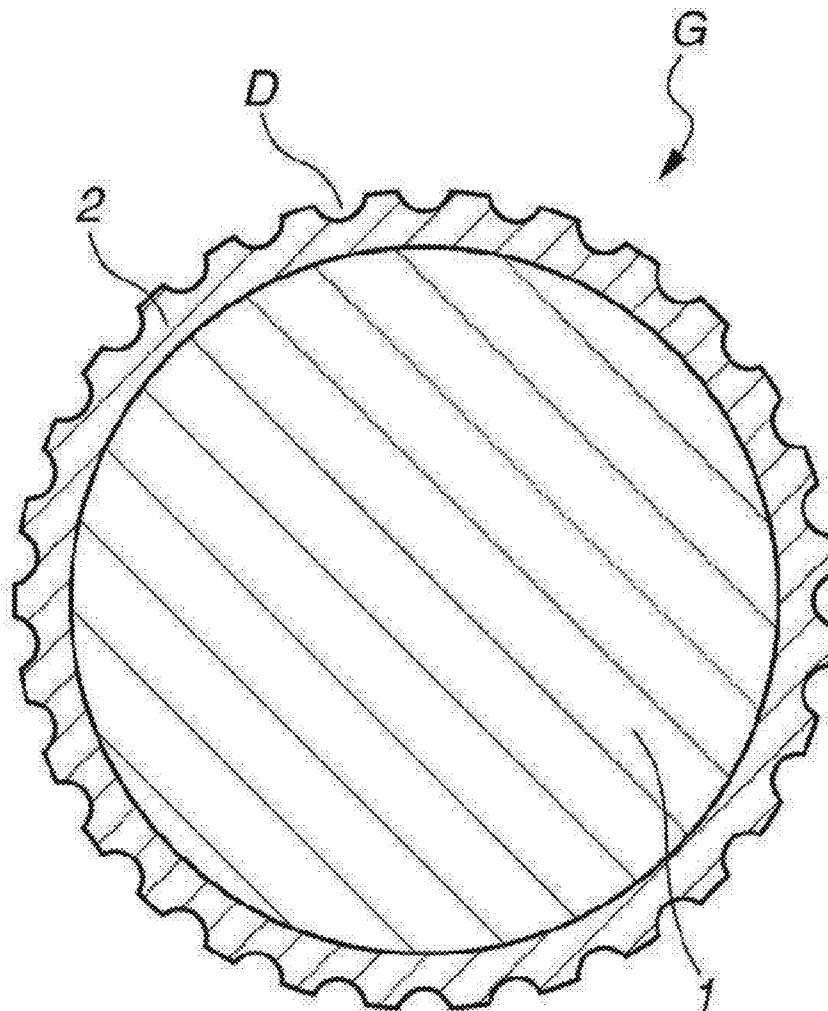
US 20140073460A1

(19) **United States**(12) **Patent Application Publication**  
**OZAWA et al.**(10) **Pub. No.: US 2014/0073460 A1**(43) **Pub. Date: Mar. 13, 2014**(54) **GOLF BALL**(52) **U.S. Cl.**

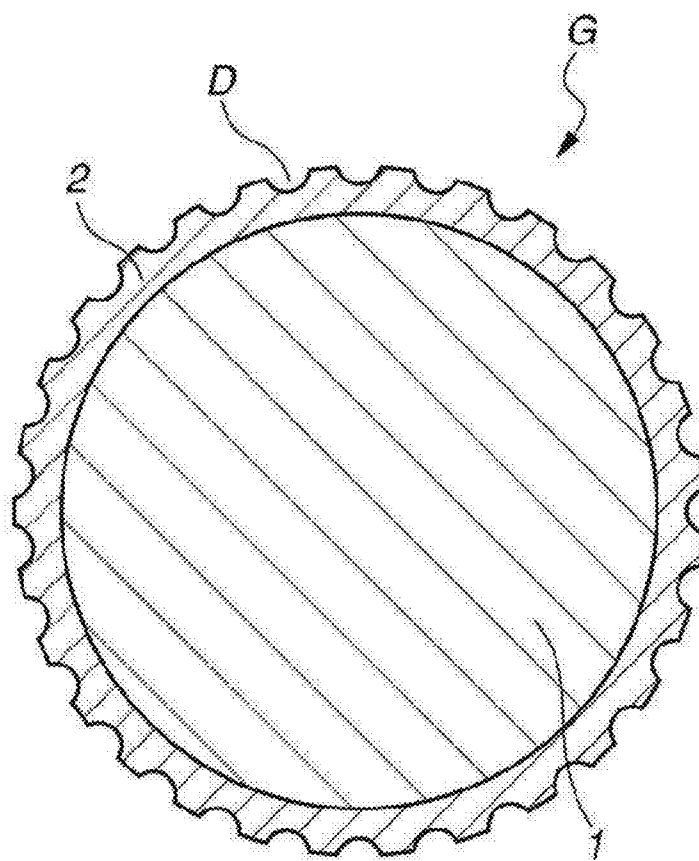
USPC ..... 473/377; 473/351

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Tokyo (JP)(21) Appl. No.: **13/606,330**(22) Filed: **Sep. 7, 2012****Publication Classification**(51) **Int. Cl.**  
**A63B 37/02** (2006.01)

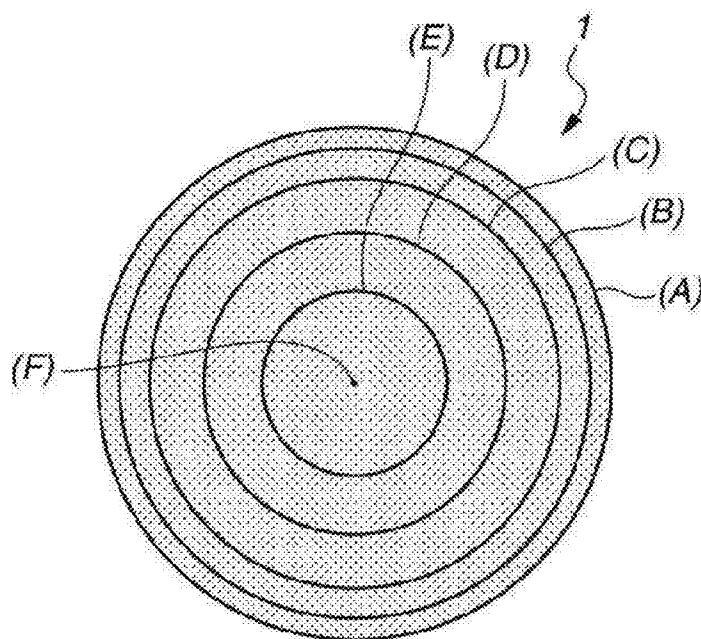
The invention provides a golf ball endowed with an improved distance and durability. The ball has a core and a cover, the core being formed of a rubber composition containing a base rubber, a co-crosslinking agent, a crosslinking initiator and a metal oxide. The base rubber is a mixture of (A) polybutadiene with (B) styrene-butadiene rubber and/or isoprene rubber, the co-crosslinking agent is methacrylic acid, and the metal oxide is zinc oxide. The rubber composition contains the crosslinking initiator in an amount of from 1.2 to 5 parts by weight per 100 parts by weight of the base rubber.



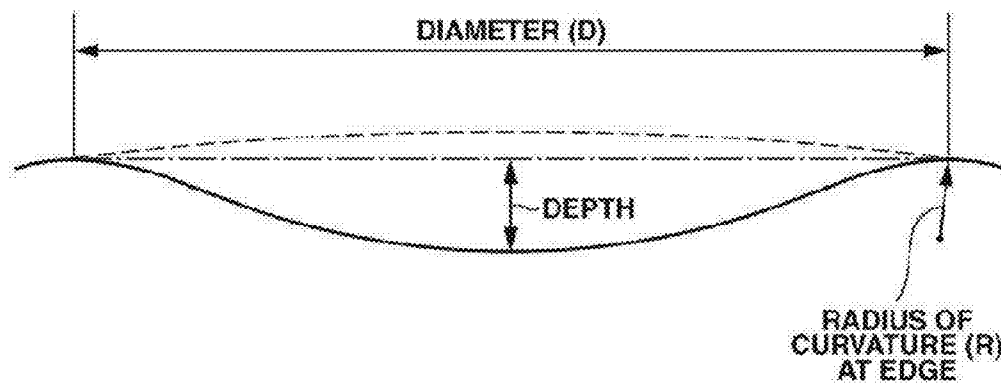
**FIG.1**



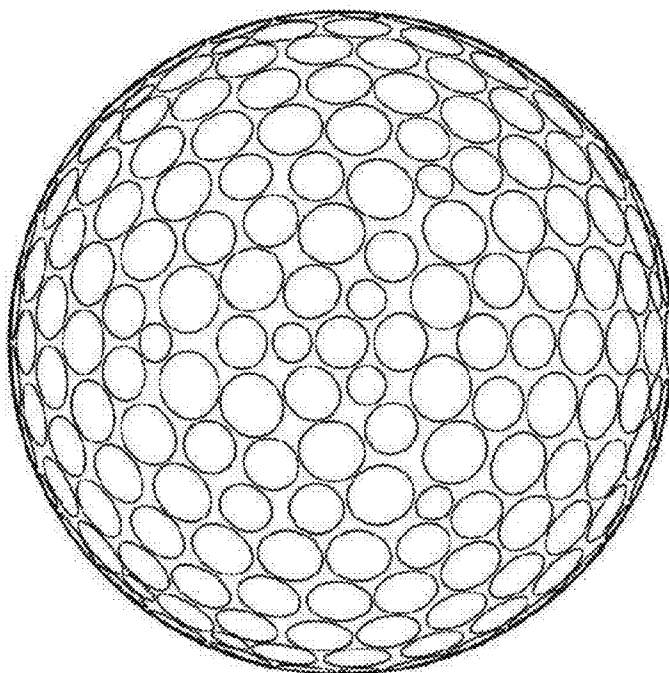
**FIG.2**



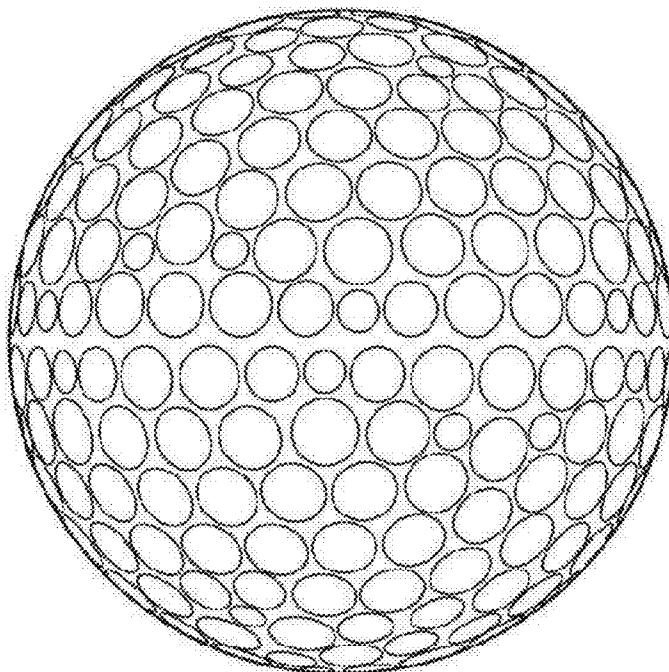
**FIG.3**



**FIG.4A**



**FIG.4B**



**FIG.5**

***BRIDGESTONE***

## GOLF BALL

### BACKGROUND OF THE INVENTION

**[0001]** The present invention relates to a golf ball composed of a core and a cover. More specifically, the invention relates to a golf ball which has a reduced spin rate and thus can achieve an increased distance, which shortens the vulcanization time for the core-forming rubber composition and thus improves productivity, and which has a good durability even in long-term use.

**[0002]** In contemplating the ball construction of golf balls intended for use in competition, to impart a flight performance and feel of the sort typically experienced when playing a round of golf, it is more desirable to use a two-piece solid golf ball than a one-piece ball. Particularly in golf balls composed of a core and a cover, conferring the ball with an increased distance owing to a reduced spin rate is one of the most desirable characteristics because it enables the game to be played with a competitive advantage.

**[0003]** As is widely known, two-piece solid golf balls are composed of a core and a cover, with the core being a rubber crosslinked material of certain desirable properties obtained by using a base rubber composed primarily of cis-1,4-polybutadiene rubber to which compounding ingredients such as a co-crosslinking agent, a metal oxide and an organic peroxide have been added. For example, JP-A 59-49779 teaches, as the rubber composition for the core of a two-piece solid golf ball, the compounding of a given amount of zinc methacrylate as a co-crosslinking agent in cis-1,4-polybutadiene rubber. However, when zinc methacrylate is used in this way in a core-forming rubber composition, achieving good ball durability in long-term use has been difficult.

**[0004]** In addition, JP-A 2003-70936, JP-A 2007-61614, JP-A 2007-301357, JP-A 2010-115485, JP-A 2010-115486, JP-A 2004-180793, JP-A 2008-149190, JP-A 2009-195761, JP-A 2005-27814, and JP-A 2010-269147 all describe, as rubber compositions for the cores of two-piece solid golf balls, the compounding of given amounts of zinc acrylate in cis-1,4-polybutadiene rubber. However, here too, when zinc acrylate is used in the core-forming rubber composition, achieving good ball durability in long-term use has been difficult.

**[0005]** Prior art relating to this invention is described in JP-A 2002-126128, which is directed at a one-piece golf ball having an optimized internal hardness profile from the surface toward the center of the ball. However, this prior-art golf ball lacks a satisfactory durability to "surface loss" when hit with the sharp portion of a clubhead, such as the leading edge of an iron.

**[0006]** In golf ball manufacturing operations, it is industrially advantageous to increase productivity by shortening the vulcanization time for the core-forming rubber composition. A solution to this challenge has also been awaited.

### SUMMARY OF THE INVENTION

**[0007]** Accordingly, the object of the present invention is to provide a golf ball which has a reduced spin rate and thus can achieve an increased distance, which shortens the vulcanization time for the core-forming rubber composition and thus improves productivity, and which has a good durability even in long-term use.

**[0008]** The inventors have conducted extensive investigations in order to attain the above objects and, as a result of

repeated improvements in core-forming rubber compositions which contain cis-1,4-polybutadiene rubber and use methacrylic acid as the co-crosslinking agent, have found that by using a mixture of (A) polybutadiene with (B) styrene-butadiene rubber and/or isoprene rubber as the base rubber, using zinc oxide as the metal oxide, and moreover increasing the amount of crosslinking initiator included to a higher than normal level of from 1.2 to 5 parts by weight per 100 parts by weight of the base rubber, the vulcanization time for the rubber composition can be shortened, enabling productivity to be increased. Moreover, the inventors have discovered that by using this rubber composition in a golf ball, the golf ball has a reduced spin rate, enabling an increased distance to be achieved, in addition to which the ball has a good durability even in long-term use.

**[0009]** In particular, according to the findings of the inventors, by adding styrene-butadiene rubber and/or isoprene rubber to the polybutadiene commonly used as the base rubber, the initial velocities of the ball and the core can easily be controlled to the desired values, thus enabling the distance to be controlled.

**[0010]** Accordingly, the invention provides the following golf balls.

[1] A golf ball comprising a core and a cover, wherein the core is formed of a rubber composition comprising a base rubber, a co-crosslinking agent, a crosslinking initiator and a metal oxide, the base rubber being a mixture of (A) polybutadiene with (B) styrene-butadiene rubber and/or isoprene rubber, the co-crosslinking agent being methacrylic acid, the metal oxide being zinc oxide, and the rubber composition containing the crosslinking initiator in an amount of from 1.2 to 5 parts by weight per 100 parts by weight of the base rubber.

[2] The golf ball of [1], wherein the rubber composition further includes a fatty acid metal salt.

[3] The golf ball of [2], wherein the fatty acid metal salt is zinc stearate.

[4] The golf ball of [2], wherein the fatty acid metal salt is included in an amount of from 0.1 to 5 parts by weight per 100 parts by weight of the base rubber.

[5] The golf ball of [1], wherein the cover is formed of a resin material which has a breaking strength of from 20 to 80 MPa and an elongation of from 150 to 600%.

[6] The golf ball of [1], wherein the core has a deflection (CH), when compressed under a final load of 1,275 N (130 kgf) from an initial load of 98 N (10 kgf), of from 2.0 to 7.0 mm.

[7] The golf ball of [1], wherein the ball has an initial velocity of not more than 76 m/s.

### BRIEF DESCRIPTION OF THE DIAGRAMS

**[0011]** FIG. 1 is a schematic cross-sectional diagram of a golf ball according to one embodiment of the invention.

**[0012]** FIG. 2 is a schematic diagram of a core illustrating positions A to F in the core hardness profile.

**[0013]** FIG. 3 is a schematic diagram showing an example of a dimple cross-section.

**[0014]** FIG. 4A is a top view and FIG. 4B is a side view showing an example of a dimple configuration.

**[0015]** FIG. 5 is a top view showing the markings that were placed on the golf balls fabricated in the examples and the comparative examples.

## DETAILED DESCRIPTION OF THE INVENTION

**[0016]** The invention is described more fully below.

**[0017]** The golf ball of the invention has a structure which, although not subject to any particular limitation, is exemplified by, as shown in FIG. 1, a two-piece solid golf ball G having a core 1 and a cover 2 that encases the core. The cover 2 has a surface on which, typically, a plurality of dimples D are formed. In the diagram, the core 1 and the cover 2 are each shown as single layers, although either or both may be composed of a plurality of layers.

**[0018]** The core is obtained by vulcanizing a rubber composition composed primarily of a rubber material. The rubber composition used to form the core includes a base rubber, a co-crosslinking agent, a crosslinking initiator and a metal oxide, and may optionally include also an antioxidant, a fatty acid metal salt and an inert filler. The base rubber used in this rubber composition is preferably a mixture of (A) polybutadiene with (B) styrene-butadiene rubber and/or isoprene rubber. In the invention, as will be subsequently described, it is desirable for the core cross-sectional hardness to change in a specific way from the surface to the center of the core, and for the core cross-sectional hardness profile to be adjusted within certain desired ranges. To this end, in formulating the core, it is essential to suitably adjust, for example, the amounts in which the various subsequently described compounding ingredients are included, the vulcanization temperature and the vulcanization time.

**[0019]** The polybutadiene (A) serving as a rubber component must have a cis-1,4 bond content of at least 60% (here and below, "%" refers to percent by weight), preferably at least 80%, more preferably at least 90%, and most preferably at least 95%. If the cis-1,4 bond content is too low, the rebound may decrease. In addition, the polybutadiene has a 1,2-vinyl bond content of preferably 2% or less, more preferably 1.7% or less, and even more preferably 1.5% or less.

**[0020]** The polybutadiene has a Mooney viscosity ( $ML_{1+4}$  (100° C.)) which is preferably at least 30, more preferably at least 35, and even more preferably at least 40, but is preferably not more than 100, more preferably not more than 80, even more preferably not more than 70, and most preferably not more than 60.

**[0021]** The term "Mooney viscosity" used herein refers to an industrial indicator of viscosity (JIS K6300) as measured with a Mooney viscometer, which is a type of rotary plastometer. This value is represented by the unit symbol  $ML_{1+4}$  (100° C.), wherein "M" stands for Mooney viscosity, "L" stands for large rotor (L-type), and "1+4" stands for a pre-heating time of 1 minute and a rotor rotation time of 4 minutes. The "100° C." indicates that measurement was carried out at a temperature of 100° C.

**[0022]** In order to obtain the rubber composition in a molded and vulcanized form having a good rebound, it is preferable for the polybutadiene to be one that has been synthesized using a rare-earth catalyst or a Group VIII metal compound catalyst.

**[0023]** The rare-earth catalyst is not subject to any particular limitation, although preferred use can be made of a catalyst which employs a lanthanum series rare-earth compound. Also, where necessary, an organoaluminum compound, an alumoxane, a halogen-bearing compound and a Lewis base may be used in combination with the lanthanum series rare-earth compound. The compounds mentioned in JP-A 11-35633, JP-A 11-164912 and JP-A 2002-293996 can be advantageously used as the various above compounds.

**[0024]** Of the above rare-earth catalysts, the use of a neodymium catalyst that employs a neodymium compound, which is a lanthanide series rare-earth compound, is especially recommended. In such a case, a polybutadiene rubber having a high cis-1,4 bond content and a low 1,2-vinyl bond content can be obtained at an excellent polymerization activity.

**[0025]** The polybutadiene has a molecular weight distribution Mw/Mn (Mw being the weight-average molecular weight, and Mn being the number-average molecular weight) of at least 1.0, preferably at least 2.0, more preferably at least 2.2, even more preferably at least 2.4, and most preferably at least 2.6. The upper limit is preferably 6.0 or less, more preferably 5.0 or less, and even more preferably 4.5 or less. If Mw/Mn is too low, the workability may decrease. On the other hand, if Mw/Mn is too high, the resilience may decrease.

**[0026]** When the above polybutadiene is used in the base rubber, the proportion of the overall rubber represented by the polybutadiene (A), although not subject to any particular limitation, is preferably at least 60 wt %, more preferably at least 62 wt %, even more preferably at least 63 wt %, and most preferably at least 65 wt %. The upper limit value is preferably not more than 99 wt %, and more preferably not more than 97 wt %.

**[0027]** Illustrative examples of cis-1,4-polybutadiene rubbers which may be used include the high-cis products BR01, BR11, BR02, BR02L, BR02LL, BR730 and BR51, all of which are available from JSR Corporation.

**[0028]** In the present invention, a styrene-butadiene rubber and/or an isoprene rubber (B) is used together with the above polybutadiene (A) as the base rubber. By thus adding (B) styrene-butadiene rubber and/or isoprene rubber to (A) polybutadiene in the base rubber, the initial velocities of the ball and core can easily be controlled to the desired values, enabling an increased distance to be achieved.

**[0029]** A solution-polymerized styrene-butadiene rubber or an emulsion-polymerized styrene-butadiene rubber may be used as the styrene-butadiene rubber (SBR) in component B. For example, use may be made of the solution-polymerized products SBR-SL552, SBR-SL555 or SBR-SL563 (available from JSR Corporation) as the solution-polymerized styrene-butadiene rubber, and use can be made of the emulsion-polymerized products SBR 1500, SBR 1502, SBR 1507 or SBR 0202 (available from JSR Corporation) as the emulsion-polymerized styrene-butadiene rubber.

**[0030]** The styrene bond content in the above styrene-butadiene rubber is preferably at least 5 wt %, more preferably at least 10 wt %, even more preferably at least 15 wt %, and most preferably at least 18 wt %. The upper limit is preferably not more than 35 wt %, more preferably not more than 30 wt %, even more preferably not more than 25 wt %, and most preferably not more than 22 wt %. If the styrene bond content is too high, due to temperature changes on account of seasonal differences, the core will become harder and large changes will occur in the rebound. On the other hand, if the styrene bond content is too low, the ease of operation during surface grinding of the core will dramatically decrease.

**[0031]** The isoprene rubber (IR) used in component B may be one having a cis-1,4-bond content of at least 60%, preferably at least 80%, and more preferably at least 90%, and having a Mooney viscosity ( $ML_{1+4}$  (100° C.)) of at least 60, preferably at least 70, and more preferably at least 80, but not more than 90, and preferably not more than 85. By way of

illustration, use may be made of, for example, the commercial product IR2200 (available from JSR Corporation).

**[0032]** The proportion of the overall base rubber accounted for by component B is preferably at least 1 wt %, more preferably at least 5 wt %, and even more preferably at least 10 wt %. The upper limit is preferably not more than 40 wt %, more preferably not more than 37 wt %, and even more preferably not more than 35 wt %. Outside of this mixing ratio, temperature changes on account of seasonal differences may cause the core to become harder and give rise to large changes in the rebound.

**[0033]** Rubber components other than above components A and B may also be used in the base rubber, insofar as the objects of the invention are attainable. Illustrative examples of such other rubber components include polybutadienes other than the above polybutadiene, and other diene rubbers such as natural rubbers and ethylene-propylene-diene rubbers.

**[0034]** Methacrylic acid is used as the co-crosslinking agent in the present invention. Here, methacrylic acid is included in an amount, per 100 parts by weight of the base rubber, of preferably at least 5 parts by weight, more preferably at least 7 parts by weight, even more preferably at least 12 parts by weight, and most preferably at least 13 parts by weight. The upper limit in the amount of methacrylic acid is preferably not more than 40 parts by weight, more preferably not more than 35 parts by weight, even more preferably not more than 30 parts by weight, and most preferably not more than 25 parts by weight. Including too much methacrylic acid may make the core too hard, giving the ball an unpleasant feel on impact. On the other hand, including too little methacrylic acid may make the core too soft, likewise giving the ball an unpleasant feel on impact.

**[0035]** It is preferable to use an organic peroxide as the crosslinking initiator. Examples of commercial products that may be advantageously used for this purpose include Percumyl D and Perhexa C40 (both from NOF Corporation), and Trigonox 29-40b (from Akzo Nobel N.V.). These may be used singly or as combinations of two or more thereof.

**[0036]** The crosslinking initiator is included in an amount, per 100 parts by weight of the base rubber, of preferably at least 1.2 parts by weight, more preferably at least 1.25 parts by weight, and even more preferably at least 1.3 parts by weight. The upper limit in the amount of crosslinking initiator is preferably not more than 5.0 parts by weight, more preferably not more than 4.0 parts by weight, and even more preferably not more than 3.5 parts by weight. Including too much crosslinking initiator may make the core too hard, giving the ball an unpleasant feel on impact and also substantially lowering the durability to cracking. On the other hand, including too little crosslinking initiator may make the core too soft, giving the ball an unpleasant feel on impact and also substantially lowering productivity.

**[0037]** Zinc oxide is used as the metal oxide in this invention. Metal oxides other than zinc oxide may be used together with the zinc oxide, insofar as the objects of the invention are attainable. The metal oxide is included in an amount, per 100 parts by weight of the base rubber, of preferably at least 5 parts by weight, more preferably at least 7 parts by weight, even more preferably at least 12 parts by weight, and most preferably at least 13 parts by weight. The upper limit in the amount of metal oxide is preferably not more than 40 parts by weight, more preferably not more than 35 parts by weight, even more preferably not more than 30 parts by weight, and

most preferably not more than 25 parts by weight. Including too much or too little may make it impossible to obtain a suitable weight and a suitable hardness and rebound.

**[0038]** An inert filler may be included in the rubber composition. Preferred use may be made of, for example, barium sulfate, calcium carbonate or silica as the inert filler. Any one of these may be used alone or two or more may be used in combination. The amount of inert filler included per 100 parts by weight of the base rubber may be set to preferably at least 1 part by weight, and more preferably at least 5 parts by weight. The upper limit in the amount of inert filler included may be set to preferably not more than 50 parts by weight, more preferably not more than 40 parts by weight, and even more preferably not more than 30 parts by weight. If the amount of inert filler included is too large or too small, a suitable weight and a good hardness and rebound may not be achieved.

**[0039]** In the practice of the invention, an antioxidant may also be included in the rubber composition. For example, use may be made of the commercial products Nocrac NS-6, Nocrac NS-30 and Nocrac 200, all available from Ouchi Shinko Chemical Industry Co., Ltd. These may be used singly or as combinations of two or more thereof.

**[0040]** The amount of antioxidant included per 100 parts by weight of the base rubber, although not subject to any particular limitation, is preferably at least 0.1 part by weight, and more preferably at least 0.15 part by weight, but is preferably not more than 1.0 part by weight, more preferably not more than 0.7 part by weight, and even more preferably not more than 0.4 part by weight. Including too much or too little antioxidant may make it impossible to achieve a suitable core hardness gradient, as a result of which a good rebound, good durability and good spin rate-lowering effect on full shots may not be achieved.

**[0041]** A fatty acid metal salt may be included in the rubber composition. By doing so, compared with conventional rubber compositions in which methacrylic acid is used as the crosslinking agent, the vulcanization time for the core-forming rubber composition is shortened, making it possible to increase productivity. Illustrative examples of the fatty acid metal salt include the zinc salts and magnesium salts of higher fatty acids such as stearic acid, palmitic acid, 12-hydroxystearic acid, behenic acid, oleic acid, linoleic acid, linolenic acid, arachidic acid, lignoceric acid, lauric acid and myristic acid. These may be used singly or two or more may be used in combination.

**[0042]** The amount of fatty acid metal salt included per 100 parts by weight of the base rubber is preferably at least 0.1 part by weight, more preferably at least 0.15 part by weight, and even more preferably at least 0.2 part by weight. The upper limit is preferably not more than 5 parts by weight, and more preferably not more than 3 parts by weight.

**[0043]** In the practice of the invention, from a resource recycling standpoint, a ground or abraded powder of vulcanized rubber may be included in a small amount of 40 parts by weight or less per 100 parts by weight of the base rubber. In this case, the ground or abraded powder may be compounded in an amount, per 100 parts by weight of the base rubber, which is more than 0 wt %, preferably at least 2 wt %, and most preferably at least 5 wt %, but is preferably not more than 40 wt %, more preferably not more than 35 wt %, even more preferably not more than 30 wt %, and most preferably not more than 25 wt %. The ground or abraded powder of vulcanized rubber is a vulcanizate which contains rubber and



unsaturated carboxylic acid or a metal salt thereof. It is desirable for the ground or abraded powder of vulcanized rubber used to have a particle size which is preferably at least 20  $\mu\text{m}$ , more preferably at least 25  $\mu\text{m}$ , and most preferably at least 30  $\mu\text{m}$ , but is preferably not more than 1,000  $\mu\text{m}$ , more preferably not more than 900  $\mu\text{m}$ , and most preferably not more than 800  $\mu\text{m}$ . Adding a crushed or abraded powder of vulcanized rubber has such effects as improving the productivity of the vulcanizate and increasing the durability to cracking. However, including too much may markedly lower the workability of the rubber composition and the productivity.

**[0044]** The core may be produced by using a known method to vulcanize and cure the rubber composition containing the various above ingredients. For example, production may be carried out by using a mixing apparatus such as a Banbury mixer or a roll mill to mix the rubber composition, compression molding or injection molding the mixed composition in a core mold, then curing the molded body by suitable heating at a temperature sufficient for the organic peroxide and co-crosslinking agent to act, such as under conditions of between about 100° C. and 200° C. for a period of from 10 to 40 minutes. The core hardness profile of the invention may be achieved by a combination of the vulcanization conditions and adjustment of the rubber formulation.

**[0045]** The core diameter, although not subject to any particular limitation, is preferably at least 38.0 mm, more preferably at least 38.9 mm, and even more preferably at least 39.3 mm, but is preferably not more than 42.1 mm, and more preferably not more than 41.1 mm. At a core diameter outside of this range, the durability of the ball to cracking may worsen dramatically and the initial velocity of the ball may decrease.

**[0046]** It is recommended that the specific gravity of the core be at least 1.05, preferably at least 1.08, and more preferably at least 1.1, but not more than 1.2, preferably not more than 1.15, and more preferably not more than 1.13.

**[0047]** The core deflection under loading, i.e., the deflection by the core when compressed under a final load of 1,275 N (130 kgf) from an initial load of 98 N (10 kgf) (which deflection is referred to here and below as “CH”), is preferably at least 2.0 mm, more preferably at least 2.3 mm, and even more preferably at least 2.4 mm, but is preferably not more than 7.0 mm, more preferably not more than 6.0 mm, even more preferably not more than 5.0 mm, and most preferably not more than 4.5 mm. If the core deflection CH is too small, the feel of the golf ball on impact may be so hard as to make the ball unpleasant to use. On the other hand, if the core deflection is too large, the feel of the golf ball on impact may be so soft as to make the ball unpleasant to use, in addition to which the productivity may decline considerably.

**[0048]** In the practice of the invention, as shown in the schematic diagram of the core in FIG. 2, letting (A) be the JIS-C hardness at a surface of the core, (B) be the JIS-C hardness at a position 2 mm in from the surface toward the center of the core, (C) be the JIS-C hardness at a position 5 mm in from the surface toward the center of the core, (D) be the JIS-C hardness at a position 10 mm in from the surface toward the center of the core, (E) be the JIS-C hardness at a position 15 mm in from the surface toward the center of the core, and (F) be the JIS-C hardness at the center of the core, the respective values (A) to (F), although not subject to any particular limitation, preferably fall within the specific ranges indicated below. By thus setting the hardness profile at the

core interior within specific ranges, both a comfortable feel on impact and also a good durability to cracking can be obtained.

**[0049]** Letting (A) be the JIS-C hardness at the surface of the core, the value of (A) is preferably at least 75, more preferably at least 76, and even more preferably at least 77, but is preferably not more than 95, more preferably not more than 93, and even more preferably not more than 91.

**[0050]** Letting (B) be the JIS-C hardness at a position 2 mm in from the surface toward the center of the core, the value of (B) is preferably at least 70, more preferably at least 73, and even more preferably at least 75, but is preferably not more than 90, more preferably not more than 87, and even more preferably not more than 85.

**[0051]** Letting (C) be the JIS-C hardness at a position 5 mm in from the surface toward the center of the core, the value of (C) is preferably at least 68, more preferably at least 70, and even more preferably at least 72, but is preferably not more than 88, more preferably not more than 86, and even more preferably not more than 84.

**[0052]** Letting (D) be the JIS-C hardness at a position 10 mm in from the surface toward the center of the core, the value of (D) is preferably at least 65, more preferably at least 66, and even more preferably at least 67, but is preferably not more than 80, more preferably not more than 78, and even more preferably not more than 76.

**[0053]** Letting (E) be the JIS-C hardness at a position 15 mm in from the surface toward the center of the core, the value of (E) is preferably at least 58, more preferably at least 59, and even more preferably at least 60, but is preferably not more than 73, more preferably not more than 71, and even more preferably not more than 69.

**[0054]** Letting (F) be the JIS-C hardness at the center of the core, the value of (F) is preferably at least 50, more preferably at least 51, and even more preferably at least 52, but is preferably not more than 65, more preferably not more than 63, and even more preferably not more than 61.

**[0055]** Moreover, in the above core hardness profile, it is preferable for the hardness relationship  $(A) > (B) \geq (C) > (D) > (E) > (F)$  to be satisfied, for the value  $(A) - (F)$  to be at least 20, for the core to be formed in such a way that (A) has the highest hardness value among (A) to (F), and for the value  $(A) - (C)$  to be in a range of from 3 to 15. If the above conditions are not satisfied, the ball may have a diminished feel on impact and a reduced durability to cracking.

**[0056]** The value of  $(A) - (C)$  has a lower limit of preferably at least 3, and more preferably at least 4, and an upper limit of preferably not more than 15, more preferably not more than 13, and even more preferably not more than 11. The value of  $(A) - (F)$  has a lower limit of preferably at least 20, and more preferably at least 21, and an upper limit of preferably not more than 50, more preferably not more than 40, and even more preferably not more than 35.

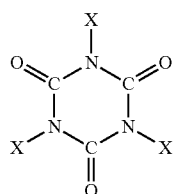
**[0057]** In the practice of the invention, the core may be subjected to surface treatment with a solution containing a haloisocyanuric acid and/or a metal salt thereof.

**[0058]** Prior to surface-treating the core with a solution containing a haloisocyanuric acid and/or a metal salt thereof, adhesion between the core surface and the adjoining cover material can be further enhanced by abrading the surface of the core (referred to below as “surface grinding”).

**[0059]** Such surface grinding removes the skin layer from the surface of the vulcanized core, and thus makes it possible to enhance the ability of the solution of haloisocyanuric acid

and/or a metal salt thereof to penetrate the core surface and also to increase the surface area of contact with the adjoining cover material. Exemplary surface grinding methods include buffing, barrel grinding and centerless grinding.

**[0060]** The haloisocyanuric acid and metal salts thereof are compounds of the following formula (I).



In the formula, X is a hydrogen atom, a halogen atom or an alkali metal atom. At least one occurrence of X is a halogen atom. Preferred halogen atoms include fluorine, chlorine and bromine, with chlorine being especially preferred. Preferred alkali metal atoms include lithium, sodium and potassium.

**[0061]** Illustrative examples of the haloisocyanuric acid and/or a metal salt thereof include chloroisocyanuric acid, sodium chloroisocyanurate, potassium chloroisocyanurate, dichloroisocyanuric acid, sodium dichloroisocyanurate, sodium dichloroisocyanurate dihydrate, potassium dichloroisocyanurate, trichloroisocyanuric acid, tribromoisocyanuric acid, dibromoisocyanuric acid, bromoisocyanuric acid, sodium and other salts of dibromoisocyanuric acid, as well as hydrates thereof, and difluoroisocyanuric acid. Of these, chloroisocyanuric acid, sodium chloroisocyanurate, potassium chloroisocyanurate, dichloroisocyanuric acid, sodium dichloroisocyanurate, potassium dichloroisocyanurate and trichloroisocyanuric acid are preferred because they are readily hydrolyzed by water to form acid and chlorine, and thus play the role of initiating addition reactions to the double bonds on the diene rubber molecules. The use of trichloroisocyanuric acid provides an especially outstanding adhesion-improving effect.

**[0062]** The haloisocyanuric acid and/or a metal salt thereof is preferably used as a solution obtained by dissolution in water or an organic solvent.

**[0063]** When water is used as the solvent, the content of the haloisocyanuric acid and/or a metal salt thereof in the treatment solution, although not subject to any particular limitation, may be set to preferably at least 0.5 part by weight, more preferably at least 1 part by weight, and even more preferably at least 3 parts by weight, per 100 parts by weight of water. If the content of haloisocyanuric acid and/or a metal salt thereof is too low, the adhesion improving effect expected after core surface treatment may not be obtained and the durability to impact may be poor. The upper limit is the saturated solution concentration. However, from the standpoint of cost effectiveness, it is preferable to set the upper limit to about 10 parts by weight per 100 parts by weight of water. The core is immersed in the treatment solution for a length of time which, although not subject to any particular limitation, may be set to preferably at least 0.3 second, more preferably at least 3 seconds, and even more preferably at least 10 seconds. The upper limit is preferably not more than 5 minutes, and more preferably not more than 4 minutes. If the immersion time is

too short, the anticipated treatment effects may not be obtained, whereas if the immersion time is too long, a loss in ball productivity may occur.

**[0064]** In cases where an organic solvent is used, a known organic solvent may be employed, with the use of an organic solvent which is soluble in water being especially preferred. Examples include ethyl acetate, acetone and methyl ethyl ketone. Of these, acetone is especially preferred on account of its ability to penetrate the core surface. The use of a water-soluble solvent is preferable because such solvents readily take up moisture; either the moisture which has been taken up readily undergoes a hydrolysis reaction with the haloisocyanuric acid and/or a salt thereof deposited on the core surface or, when water washing is used in a subsequent step, the affinity of water to the core surface increases, along with which a hydrolysis reaction between the water and the haloisocyanuric acid and/or a metal salt thereof more readily arises.

**[0065]** When dissolved in an organic solvent, the content of the haloisocyanuric acid and/or a metal salt thereof in the solution is preferably at least 0.3 wt %, more preferably at least 1 wt %, and even more preferably at least 2.5 wt %. At less than 0.3 wt %, the adhesion improving effect anticipated following core surface treatment may not be obtained, possibly resulting in a poor durability to impact. The upper limit in the content may be as high as the saturated solution concentration. However, from the standpoint of cost effectiveness, when prepared as an acetone solution, for example, setting the upper limit in content to about 10 wt % is preferred. The core is immersed in the solution for a length of time which is preferably at least 0.3 second, more preferably at least 3 seconds, and even more preferably at least 10 seconds. The upper limit is preferably not more than 5 minutes, and more preferably not more than 4 minutes. If the immersion time is too short, the desired effects of treatment may not be obtained, whereas if the immersion time is too long, a loss in ball productivity may occur.

**[0066]** The method of treating the core surface with a haloisocyanuric acid and/or a metal salt thereof is exemplified by methods which involve coating the surface of the core with a solution of haloisocyanuric acid and/or a metal salt thereof by brushing or spraying on the solution, and methods in which the core is immersed in a solution of the haloisocyanuric acid and/or a metal salt thereof. From the standpoint of productivity and high penetrability of the core surface by the solution, the use of an immersion method is especially preferred.

**[0067]** After the core has been surface treated with a solution containing haloisocyanuric acid and/or a metal salt thereof, it is preferable to wash the surface of the core with water. Water washing of the core surface may be carried out by a method such as running water, spraying, or soaking in a washing tank. However, because the aim here is not merely to wash, but also to initiate and promote the desired treatment reactions, the washing method should be one that is not too vigorous. Accordingly, preferred use may be made of washing by soaking in a washing tank. In such a case, it is desirable to place the cores to be washed from about one to five times in a washing tank that has been filled with fresh water.

**[0068]** Treating the core surface with a haloisocyanuric acid and/or a metal salt thereof greatly improves adhesion between the core surface and the cover. The reason for this is not well understood, but is thought to be as follows.

[0069] First, the haloisocyanuric acid and/or a metal salt thereof, together with the solvent, penetrates to the interior of the diene rubber making up the core and approaches the vicinity of the double bonds on the backbone. Water then enters the core surface, whereupon the haloisocyanuric acid and/or a metal salt thereof is hydrolyzed by the water, releasing the halogen. The halogen attacks a double bond on the diene rubber backbone located nearby, as a result of which an addition reaction proceeds. In the course of this addition reaction, the liberated isocyanuric acid is added, together with the halogen, to the diene rubber backbone while retaining its cyclic structure.

[0070] The added isocyanuric acid has three —NHCO— structures on the molecule.

[0071] Because —NHCO— structures are thereby conferred to the core surface that has been treated with the haloisocyanuric acid and/or a metal salt thereof, adhesion with the cover material improves further. It is most likely because of this that the durability of the golf ball to impact improves. Moreover, when a polyurethane elastomer or polyamide elastomer having the same —NHCO— structures on the polymer molecules is used as the cover material, the affinity increases even further, presumably increasing the durability to impact.

[0072] Following surface treatment, when the material at the surface portion of the solid core is examined by differential scanning calorimetry (DSC), no exothermic or endothermic peaks are observed from room temperature to 300° C. This means that the functional groups which have been introduced maintain a stable state within this temperature range. In other words, during molding of the cover material, the functional groups which have been introduced do not undergo degradation or the like due to heat, and thus continue to be effective. Also, because melting in the manner of a hot melt resin does not arise, deleterious effects on durability and quality of appearance, such as resin bleed out to the parting line, do not occur. In addition, the very fact that the material in the surface portion of the solid core following the surface treatment described above is stable may be regarded as evidence that the isocyanuric acid having a melting point above 300° C. has been added with its molecular structure still intact.

[0073] In cases where, using an organic solvent, the addition of isocyanuric acid and chlorine to the surface of diene rubber has occurred, changes in the bonding states before and after addition appear in an infrared absorption spectrum as increases in the C=O bond (stretching) absorption peak at 1725 to 1705 cm<sup>-1</sup>, the broad N—H bond (stretching) absorption peak at 3450 to 3300 cm<sup>-1</sup>, and the C—Cl bond absorption peak at 800 to 600 cm<sup>-1</sup>. Hence, by measuring the IR absorption spectrum of a surface-treated core and confirming increases in these absorption peaks, it is possible to qualitatively confirm that isocyanuric acid and chlorine addition to diene rubber molecules at the core surface has indeed occurred.

[0074] Next, the material making up the cover which directly encases the core is described.

[0075] No particular limitation is imposed on the cover resin material in this invention, provided the material has a breaking strength of from 20 to 80 MPa and an elongation of from 150 to 600%. However, preferred use may be made of an ionomer resin or a thermoplastic resin such as polyurethane. The use of a resin material composed primarily of polyurethane is especially preferred. For example, use may be made

of a thermoplastic polyurethane elastomer or a thermoset polyurethane resin, with the use of a thermoplastic polyurethane elastomer being especially preferred.

[0076] The breaking strength of the cover resin material is at least 20 MPa, preferably at least 25 MPa, more preferably at least 30 MPa, and most preferably at least 35 MPa, but not more than 80 MPa, preferably not more than 75 MPa, more preferably not more than 70 MPa, and most preferably not more than 65 MPa. The elongation of the cover resin material is at least 150%, preferably at least 200%, and more preferably at least 250%, but not more than 600%, preferably not more than 550%, more preferably not more than 520%, and most preferably not more than 490%. The breaking strength and elongation (tensile tests) are measured by methods in general accordance with JIS K 7311-1995. By using such a cover resin material having a breaking strength and an elongation in the above-indicated ranges, the durability to cracking, durability to surface loss and durability to abrasion desired of a practice golf ball intended for long-term use can be improved.

[0077] The thermoplastic polyurethane elastomer has a structure composed of soft segments formed from a polymeric polyol (polymeric glycol) and hard segments formed from a chain extender and a diisocyanate. Here, the polymeric polyol serving as a starting material may be any which has hitherto been used in the art relating to thermoplastic polyurethane materials, and is not subject to any particular limitation. Exemplary polymeric polyols include polyester polyols and polyether polyols. Polyether polyols are more preferable than polyester polyols because they enable thermoplastic polyurethane materials having a high rebound resilience and excellent low-temperature properties to be synthesized. Illustrative examples of polyether polyols include polytetramethylene glycol and polypropylene glycol. Polytetramethylene glycol is especially preferred from the standpoint of the rebound resilience and the low-temperature properties. The polymeric polyol has an average molecular weight of preferably from 1,000 to 5,000. To synthesize a thermoplastic polyurethane material having a high rebound resilience, an average molecular weight of from 2,000 to 4,000 is especially preferred.

[0078] The chain extender employed is preferably one which has hitherto been used in the art relating to thermoplastic polyurethane materials. Illustrative examples include, but are not limited to, 1,4-butylene glycol, 1,2-ethylene glycol, 1,3-butanediol, 1,6-hexanediol and 2,2-dimethyl-1,3-propanediol. These chain extenders have an average molecular weight of preferably from 20 to 15,000.

[0079] The diisocyanate employed is preferably one which has hitherto been used in the art relating to thermoplastic polyurethane materials. Illustrative examples include, but are not limited to, aromatic diisocyanates such as 4,4'-diphenylmethane diisocyanate, 2,4-toluene diisocyanate and 2,6-toluene diisocyanate, and aliphatic diisocyanates such as hexamethylene diisocyanate. Depending on the type of isocyanate, control of the crosslinking reaction during injection molding may be difficult. In this invention, the use of 4,4'-diphenylmethane diisocyanate, which is an aromatic diisocyanate, is most preferred.

[0080] A commercial product may be advantageously used as the thermoplastic polyurethane material composed of the above materials. Illustrative examples include those available under the trade names Pandex T8180, Pandex T8195, Pandex T8290, Pandex T8295 and Pandex T8260 (all available from

DIC Bayer Polymer, Ltd.), and those available under the trade names Resamine 2593 and Resamine 2597 (available from Dainichiseika Color & Chemicals Mfg. Co., Ltd.).

**[0081]** The cover has a thickness which is preferably at least 0.3 mm, more preferably at least 0.5 mm, and even more preferably at least 0.7 mm, but is preferably not more than 1.9 mm, more preferably not more than 1.8 mm, and even more preferably not more than 1.7 mm. If the cover thickness is larger than the above range, the ball rebound may decrease and the flight performance may worsen. On the other hand, if the cover thickness is smaller than the above range, the durability to cracking may decrease. In particular, when the ball is hit thin, or "topped," the cover may tear.

**[0082]** The cover has a specific gravity which is preferably at least 1.13, more preferably at least 1.14, and even more preferably at least 1.15, but is preferably not more than 1.30, more preferably not more than 1.20, and even more preferably not more than 1.17.

**[0083]** The cover material has a Shore D hardness which is preferably at least 30, more preferably at least 35, and even more preferably at least 38, but is preferably not more than 57, more preferably not more than 55, even more preferably not more than 53, still more preferably not more than 51, and most preferably not more than 48. If the Shore D hardness of the cover is higher than the above range, the appearance performance in long-term use (durability of markings) may decline, in addition to which the flight performance may markedly decrease. On the other hand, if the Shore D hardness of the cover is lower than the above range, the durability to cracking may markedly decrease and, particularly when the ball is topped, the cover may tear. In addition, the spin rate may become very high, possibly shortening the distance traveled by the ball.

**[0084]** The golf ball of the invention typically has numerous dimples formed on the surface thereof, each dimple having a spatial volume below a flat plane circumscribed by an edge of the dimple. Although not subject to any particular limitation, the sum of the dimple spatial volumes, expressed as a ratio (VR) with respect to the volume of a hypothetical sphere representing the ball were it to have no dimples on the surface thereof, is preferably in a range of from 0.8 to 1.7, the lower limit being more preferably 0.83, even more preferably 0.85, and most preferably 0.86, and the upper limit being more preferably 1.5, even more preferably 1.3, and most preferably 1.2.

**[0085]** Also, although not subject to any particular limitation, the dimples formed on the golf ball of the invention preferably satisfy conditions (1) and (2) below. Although satisfying both of the following conditions (1) and (2) at the same time is preferred, it is acceptable for either one of these conditions alone to be satisfied.

**[0086]** First, referring to FIG. 3, as condition (1), it is preferable for the dimples to have a peripheral edge provided with a roundness represented by a radius of curvature R in a range of from 0.5 to 2.5 mm. The lower limit of the radius of curvature R is more preferably 0.6 mm, and even more preferably 0.7 mm, and the upper limit is more preferably 1.8 mm, and even more preferably 1.5 mm.

**[0087]** Next, as condition (2), it is preferable for the ratio ER of a collective number of dimples RA having a radius of curvature R to diameter D ratio (R/D) of at least 20%, divided by a total number of dimples N on the surface of the ball, to be in a range of from 15 to 95%. Here, the ratio R/D is expressed as a percentage (R/D×100%), a larger value indicating a

dimple in which the rounded part of the dimple accounts for a larger proportion of the dimple size and which has a smoother cross-sectional shape. The ratio ER indicates the number of such smooth dimples as a proportion of the total number of dimples; by setting ER in a range of from 15 to 95%, damage to the paint film at dimple edges can be effectively suppressed. The upper limit in the ratio R/D is preferably not more than 60%, and more preferably not more than 40%. The lower limit in the ratio ER is more preferably 20%, and even more preferably 25%, and the upper limit is more preferably 90%, even more preferably 85%, and most preferably 70%.

**[0088]** Also, although not subject to any particular limitation, it is preferable for condition (3) to be satisfied. That is, as condition (3), it is preferable for the ball to have thereon a plurality of dimple types of differing diameter, and for the ratio DER of a combined number of dimples DE obtained by adding together dimples having an own diameter and having an own radius of curvature larger than or equal to a radius of curvature of dimples of larger diameter than the own diameter plus dimples of a type having a largest diameter, divided by the total number N of dimples on the surface of the ball, to be at least about 80%.

**[0089]** Generally, at a fixed dimple depth (see FIG. 3), the radius of curvature R representing the roundness provided to the peripheral edges of the dimples is smaller at smaller dimple diameters. However, above condition (3), by such means as adjusting the depth, sets the radius of curvature R representing the roundness of the peripheral edge to be as large as possible even in dimples having a small diameter, thus forming dimples having a smooth cross-sectional shape, and also increases the proportion of such smooth dimples by setting the above ratio DER to at least 80%, in this way more effectively suppressing damage to the paint film. The ratio DER is more preferably at least 85%, even more preferably at least 90%, and most preferably at least 93%. The upper limit in the ratio DER is 100%.

**[0090]** In addition, the dimples on the golf ball of the invention, although not subject to any particular limitation, preferably satisfy conditions (4) to (6) below. Although it is preferable for all of the following conditions (4) to (6) to be satisfied at the same time, it is acceptable for any one of these conditions alone to be satisfied.

**[0091]** First, as condition (4), it is preferable for the number of dimple types of differing diameter D on the ball to be 3 or more, and more preferable for dimples of at least five types to be formed. In this case, the diameters D of the dimples, although not subject to any particular limitation, are preferably set in a range of from 1.5 mm to 7 mm, the lower limit being more preferably 1.8 mm and the upper limit being more preferably 6.5 mm. The depths of the dimples, although likewise not subject to any particular limitation, are preferably set in a range of from 0.05 mm to 0.35 mm, the lower limit being more preferably 0.1 mm and the upper limit being more preferably 0.3 mm, and even more preferably 0.25 mm.

**[0092]** As condition (5), the total number N of dimples on the surface of the ball is preferably not more than 380, and more preferably not more than 350. The total number N of dimples is even more preferably in a range of from 220 to 340.

**[0093]** As condition (6), it is preferable for the dimples to be formed in such a way that the surface coverage SR of the dimples, which is the sum of individual dimple surface areas, each defined by a flat plane circumscribed by an edge of the dimple (dash-dot line in FIG. 3), expressed as a percentage of

the surface area of a hypothetical sphere representing the ball were it to have no dimples on the surface thereof (broken line in FIG. 3), is from 60 to 74%. At a surface coverage SR greater than 74%, the intervals between neighboring dimples become too narrow, which may make it difficult to provide the dimple edges with a roundness having the radius of curvature specified in above condition (1). On the other hand, at a surface coverage SR below 60%, the aerodynamic performance decreases, as a result of which the distance traveled by the ball may decrease. The surface coverage SR has a lower limit of more preferably 65%, and even more preferably 68%, and an upper limit of more preferably 73%.

**[0094]** In one-piece golf balls, because rubber has a somewhat yellow color, a white enamel paint is generally applied as a first coat, following which a clear paint is applied. In the inventive ball, in order to ensure a good appearance, it is preferable to apply a clear paint to the surface of the ball. The resulting clear coat has a thickness at dimple lands (Y) which is at least 10  $\mu\text{m}$ , preferably at least 12  $\mu\text{m}$ , and most preferably at least 13  $\mu\text{m}$ , but is not more than 30  $\mu\text{m}$ , preferably not more than 25  $\mu\text{m}$ , and most preferably not more than 20  $\mu\text{m}$ ; and a thickness at dimple edges (Z) which is at least 8  $\mu\text{m}$ , preferably at least 10  $\mu\text{m}$ , and most preferably at least 11  $\mu\text{m}$ , but is not more than 28  $\mu\text{m}$ , preferably not more than 23  $\mu\text{m}$ , and most preferably not more than 18  $\mu\text{m}$ . Also, the ratio Z/Y of edge areas (Z) to land areas (Y), expressed as a percentage (Z/Y $\times$ 100), is at least 60%, preferably at least 70%, and most preferably at least 80%, but is not more than 100%, and preferably not more than 95%. Outside the above range, the durability of markings at dimple edges decreases dramatically in long-term use.

**[0095]** The ball diameter is at least 42 mm, preferably at least 42.3 mm, and more preferably at least 42.67 mm, but is not more than 44 mm, preferably not more than 43.8 mm, more preferably not more than 43.5 mm, and even more preferably not more than 43 mm.

**[0096]** The ball weight is preferably at least 44.5 g, more preferably at least 44.7 g, even more preferably at least 45.1 g, and most preferably at least 45.2 g, but is preferably not more than 47.0 g, more preferably not more than 46.5 g, and even more preferably not more than 46.0 g.

**[0097]** The ball deflection (BH) when compressed under a final load of 1,275 N (130 kgf) from an initial load of 98 N (10 kgf) is preferably at least 2.0 mm, more preferably at least 2.3 mm, and even more preferably at least 2.4 mm, but is preferably not more than 7.0 mm. Moreover, when the core and ball are each compressed under a final load of 1,275 N (130 kgf) from an initial load of 98 N (10 kgf), the ratio CH/BH of the respective deflections CH and BH is preferably at least 0.95, more preferably at least 0.96, and even more preferably at least 0.97, but is preferably not more than 1.1, more preferably not more than 1.08, and even more preferably not more than 1.07. If the ratio CH/BH is too large, the hardness (deflection) of the finished ball will be very hard relative to the core hardness (deflection). That is, because the cover becomes harder, the feel on impact may decrease and the

quality of the appearance may decline with long-term use. On the other hand, if the ratio CH/BH is too small, the cover will be very soft, which may significantly lower the durability to cracking and lead to cracking of the cover, particularly when the ball is topped. In addition, the spin rate may undergo a large increase, which may result in a shorter distance of travel by the ball.

**[0098]** Moreover, in the invention, the finished ball has an initial velocity (BV) with a lower limit of preferably at least 70 m/s, more preferably at least 70.5 m/s, and even more preferably at least 71 m/s. The upper limit is preferably not more than 76 m/s, more preferably not more than 75.7 m/s, and even more preferably not more than 75.4 m/s. If the initial velocity (BV) of the finished ball falls outside of the above range, this may have an undesirable effect such as a drastically reduced distance or, conversely, excessive travel by the ball.

**[0099]** Moreover, from the standpoint of ensuring a good durability over a long period of time, the golf ball of the invention, upon initial measurement, has a deflection BH1 (mm) when compressed under a final load of 1,275 N (130 kgf) from an initial load of 98 N (10 kgf) and an initial velocity BV1 (m/s) and, when measured again after being left to stand for 350 days following initial measurement, has a deflection BH2 (mm) when compressed under a final load of 1,275 N (130 kgf) from an initial load of 98 N (10 kgf) and an initial velocity BV2 (m/s), such that the difference BH2–BH1 is preferably not more than 0.2 mm, more preferably not more than 0.15 mm, and even more preferably not more than 0.1 mm, and such that the difference BV2–BV1 is preferably not more than 0.3 m/s, more preferably not more than 0.2 m/s, and even more preferably not more than 0.1 m/s.

**[0100]** As described above, the golf ball of the invention has a reduced spin rate and can thus achieve an increased distance. Moreover, the inventive ball shortens the vulcanization time of the core-forming rubber composition, thus improving productivity, and has a good durability even in long-term use.

## EXAMPLES

**[0101]** The following Examples and Comparative Examples are provided to illustrate the invention, and are not intended to limit the scope thereof.

Examples 1 to 4, Comparative Examples 1 to 10

**[0102]** Rubber materials formulated as shown in Table 1 below were furnished for the fabrication of golf balls in the Examples and Comparative Examples. These rubber compositions were suitably mixed using a kneader or roll mill, then vulcanized under the temperature and time conditions in Table 1 to produce solid cores in the respective examples. Ingredient amounts in the table below are shown in parts by weight.

TABLE 1

parts by weight		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10
Core formulation	BR01	80	80	80	80	100	100	100	100		95
	IR2200	20		12.5	5						5
	SBR SL563		20	7.5	15						
	BR730										

TABLE 1-continued

parts by weight	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10
Perhexa C-40 (40% dilution)							0.6	0.6	0.6	
Actual amount of addition							0.24	0.24	0.24	
Percumyl D	1.3	1.3	1.3	1.3	1.07	0.8	0.6	0.6	0.6	1.07
Zinc oxide	22.5	22.5	22.5	22	23	23	6	6	9.5	23
Antioxidant	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2
Methacrylic acid	23.5	23.5	23.5	22	22.5	22.5				22.5
Zinc methacrylate							33			
Zinc acrylate								33	26	
Zinc stearate	1.7	1.7	1.7	1.7						
Titanium oxide										4
Vulcanization conditions	Temperature (° C.)	170	170	170	170	170	160	160	160	170
	Time (minutes)	18	18	18	18	20	20	13	13	30

[0103] Details on the materials used in the core formulations in the above table are provided below.

[0104] (1) BR01: A butadiene rubber synthesized with a nickel catalyst, available from JSR Corporation; Mooney viscosity ML, 46

[0105] (2) IR2200: An isoprene rubber, available from JSR Corporation; Mooney viscosity ML, 82

[0106] (3) SBR SL563: A solution-polymerized styrene-butadiene rubber, available from JSR Corporation; styrene bond content, 20%

[0107] (4) BR730: A butadiene rubber synthesized with a neodymium catalyst, available from JSR Corporation; Mooney viscosity ML, 55

[0108] (5) Perhexa C-40: An organic peroxide, available from NOF Corporation

[0109] (6) Percumyl D: An organic peroxide, available from NOF Corporation

[0110] (7) Zinc oxide: Available from Sakai Chemical Co., Ltd.

[0111] (8) Antioxidant: "Nocrac NS-6," available from Ouchi Shinko Chemical Industry Co., Ltd.

[0112] (9) Methacrylic acid: Available from Kuraray Co., Ltd.

[0113] (10) Zinc methacrylate: Available from Asada Chemical Industry Co., Ltd.

[0114] (11) Zinc acrylate: Available from Nihon Jyoryu Kogyo Co., Ltd.

[0115] (12) Titanium oxide: Available from Ishihara Sangyo Kaisha, Ltd.

[0116] In each example, after the rubber composition formulated from the ingredients shown in Table 1 was molded and vulcanized to form a core, the surface of the core was abraded to a desired diameter. Next, surface treatment of the core was carried out by immersing the core for 30 seconds in an acetone solution of trichloroisocyanuric acid (concentration, 3 wt %), then washing the surface of the core with water. The core was subsequently set in a mold for injection-molding the cover, and the cover composition shown in Table 2 below was injection-molded over the solid core.

TABLE 2

		A	C	D
Formulation	Himilan 1557		50	
(pbw)	Himilan 1601		50	
	Himilan AM7327			50
	Surlyn 6320			50

TABLE 2-continued

	A	C	D
Pandex T8260			
Pandex T8195	100		
Magnesium stearate		1	1
Titanium dioxide	3.5	2.1	2.1
Polyethylene wax	1.5		

[0117] Details on the materials used in the cover composition in the above table are provided below.

[0118] "Himilan": Ionomer resins available under this trade name from DuPont-Mitsui Polychemicals Co., Ltd.

[0119] "Pandex": Thermoplastic polyurethane elastomers available under this trade name from DIC Bayer Polymer, Ltd.

[0120] "Surlyn": An ionomer resin available under this trade name from E.I. DuPont de Nemours & Co.

[0121] Magnesium stearate: Available from NOF Corporation

[0122] Titanium dioxide: Available under the trade name "Tippaque R550" from Ishihara Sangyo Kaisha, Ltd.

[0123] Polyethylene wax: Available under the trade name "Sanwax 161P" from Sanyo Chemical Industries, Ltd.

[0124] In order to form a predetermined dimple pattern on the surface of the cover, a plurality of protrusions corresponding to the dimple pattern were formed in the mold cavity, by means of which dimples were impressed onto the surface of the cover at the same time that the cover was injection-molded. Details on the dimples are given below in Table 3. The markings shown in FIG. 5 were printed on the ball surface. In addition, the ball was clear-coated with a paint composed of 100 parts by weight of polyester resin (acid value, 6; hydroxyl value, 168) (solids)/butyl acetate/propylene glycol monomethyl ether acetate (PMA) in a weight ratio of 70/15/15 as the base; 150 parts by weight of a non-yellowing polyisocyanate, specifically an adduct of hexamethylene diisocyanate (available from Takeda Pharmaceutical Co., Ltd. as Takenate D-160N; NCO content, 8.5 wt %; solids content, 50 wt %) as the curing agent; and 150 parts by weight of butyl acetate. In Comparative Example 11, a coating of white enamel paint was applied as a base coat for clear coating.

TABLE 3

	Dimple No.	Number	Diameter D (mm)	Depth (mm)	R (mm)	R/D ratio	N (number)	RA (number)	ER (%)	DE (number)	DER (%)	SR	VR	Configuration
Dimple I	1	24	4.4	0.182	0.75	17	338	102	30	330	98	72	0.86	FIG. 4
	2	204	4.2	0.175	0.8	19								
	3	66	3.6	0.165	0.8	22								
	4	12	2.7	0.135	0.9	33								
	5	24	2.5	0.105	0.9	36								
	6	8	3.4	0.145	0.6	18								
Dimple II	1	24	4.4	0.216	0.5	11	338	36	11	306	91	72	0.99	FIG. 4
	2	204	4.2	0.209	0.5	12								
	3	66	3.6	0.194	0.6	17								
	4	12	2.7	0.151	0.6	22								
	5	24	2.5	0.116	0.5	20								
	6	8	3.4	0.160	0.5	15								

[0125] The abbreviations and symbols relating to dimples which appear in Table 3 are explained below.

[0126] R: Radius of curvature representing roundness provided at the peripheral edge of a dimple

[0127] R/D ratio: Ratio of radius of curvature R to diameter D

[0128] N: Total number of dimples

[0129] RA: Collective number of dimples having an R/D ratio of at least 20%

[0130] ER: Ratio of RA to total number of dimples N

[0131] DE: Sum of the number of dimples having an own diameter and having an own radius of curvature larger than or equal to a radius of curvature of dimples of larger diameter than the own diameter, plus the number of dimples of a type having a largest diameter

[0132] DER: Ratio of DE to the total number of dimples N

[0133] SR: Sum of individual dimple surface areas, each defined by a flat plane circumscribed by an edge of the dimple, expressed as a percentage of the surface area of a hypothetical sphere representing the ball were the ball to have no dimples on the surface thereof.

[0134] VR: Sum of individual dimple spatial volumes, each formed below a flat plane circumscribed by an edge of the dimple, expressed as a percentage of the volume of a hypothetical sphere representing the ball were the ball to have no dimples on the surface thereof

[0135] The physical properties of the cores and covers in the respective examples of the invention and the comparative examples, and the physical properties, distance, durability and feel of the golf balls obtained in each example were measured or evaluated as described below. The results are presented in Table 4.

#### Deflection of Core and Finished Ball (mm)

[0136] The deflections (mm) of, as the test spheres, the cores and finished balls when compressed at a rate of 10 mm/min under a final load of 1,275 N (130 kgf) from an initial load of 98 N (10 kgf) were measured. The tests were performed using a model 4204 test system from Instron Corporation.

#### Cross-Sectional Hardness of Core

[0137] The core was cut with a fine cutter and the JIS-C hardnesses at above positions B to F were measured in accordance with JIS K6301-1975 after holding the core isothermally at  $23\pm 1^\circ\text{C}$ . (at two places in each of N=5 samples).

#### Surface Hardness of Core

[0138] JIS-C hardness measurements were carried out on the core surface in accordance with JIS K6301-1975 after holding the core isothermally at  $23\pm 1^\circ\text{C}$ . (at two places in each of N=5 samples).

#### Rebound of Core and Finished Ball (Initial Velocity)

[0139] The initial velocity was measured using an initial velocity measuring apparatus of the same type as the USGA drum rotation-type initial velocity instrument approved by the R&A. The cores and balls used as the samples were held isothermally at a temperature of  $23\pm 1^\circ\text{C}$ . for at least 3 hours, then tested in a room temperature ( $23\pm 2^\circ\text{C}$ .) chamber. Ten samples were each hit twice, and the time taken for the samples to traverse a distance of 6.28 ft (1.91 m) was measured and used to compute the initial velocity.

#### Cover Material Hardness

[0140] A cover sheet was formed and, after holding the samples isothermally at  $23\pm 1^\circ\text{C}$ ., the Shore D hardness was measured in accordance with ASTM D-2240.

#### Breaking Strength and Elongation (Tensile Tests)

[0141] The resin materials and rubber materials were formed into 2 mm thick sheets, and held in a  $23\pm 1^\circ\text{C}$ . atmosphere for two weeks. These samples were shaped into dumb-bell-shaped test specimens in accordance with JIS K 7311-1995, and the specimens were subjected to measurement in a  $23\pm 2^\circ\text{C}$ . atmosphere at a test rate of 5 mm/s, also in accordance with JIS K 7311-1995. The average breaking strength and elongation of each material were calculated from the measured values for five specimens.

#### Measurement of Coat Thickness

[0142] Lands (Y): The thickness of the clear coat at land areas at intermediate positions between dimples was measured.

[0143] Edges (Z): The thickness of the clear coat at dimple edge areas was measured.

[0144] The above measurements were carried out at three places on each of two balls in the respective examples, and the average of these measurements was determined.

## Distance

[0145] A TourStage X-Drive 701 (loft angle, 9°), manufactured by Bridgestone Sports Co., Ltd., was mounted as the driver (W#1) on a golf swing robot and the ball was struck at a head speed (HS) of 45 m/s. Both the spin rate of the ball immediately after impact and the total distance traveled by the ball were measured.

[0146] In addition, the total distance of the ball was measured again following the marking durability test above.

## Durability to Cracking

[0147] The durability of the golf ball to cracking was evaluated using an ADC Ball COR Durability Tester produced by Automated Design Corporation (U.S.). This tester functions so as to fire a golf ball pneumatically and cause it to repeatedly strike two metal plates arranged in parallel. The incident velocity against the metal plates was set at 43 m/s. The num-

ber of shots required until the golf ball cracked was measured, and the average value for five golf balls (N=5) was determined.

## Abrasion Test

[0148] Ten golf balls and 3 liters of bunker sand were placed in a magnetic ball mill having an 8 liter capacity and mixing was carried out for 144 hours, following which the balls were visually examined for any loss of markings and to assess the degree of surface scratching and the degree of loss of luster due to abrasion by the sand, as well as the degree of sand adhesion. The ball appearance was rated as "Good," "Fair" or "NG."

## Feel

[0149] Ten teaching professionals hit the test balls with a driver (W#1) and rated the feel of the balls on impact as Good, somewhat hard (Fair), or too hard (NG).

TABLE 4

		Example				Comparative Example		
		1	2	3	4	1	2	3
Core	Type	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 5
	Diameter, mm	39.9	39.9	39.9	39.9	39.9	39.9	38.5
	Specific gravity	1.12	1.13	1.13	1.12	1.12	1.12	1.12
	Deflection under 10-130 kg compression (CH), mm	3.2	2.85	2.9	2.85	2.6	3	2.6
	Rebound (CV)	74.3	74.7	74.6	74.5	74.9	74.3	74.9
	JIS-C hardness at core surface (A)	81	86	83	85	81	73	81
	JIS-C hardness 2 mm inside core surface (B)	77	81	77	81	76	65	76
	JIS-C hardness 5 mm inside core surface (C)	76	79	75	78	79	70	79
	JIS-C hardness 10 mm inside core surface (D)	67	74	69	73	74	70	74
	JIS-C hardness 15 mm inside core surface (E)	62	65	64	66	69	68	69
	JIS-C hardness at core center (F)	56	58	57	58	66	65	66
	JIS-C hardness difference between core surface and 5 mm inside core surface (A - C)	5	7	8	7	2	3	2
	JIS-C hardness difference between core surface and center (A - F)	25	28	26	27	15	8	15
Cover	Type	A	A	A	A	A	A	A
	Shore D hardness	45	45	45	45	45	45	45
	Breaking strength, MPa	40	40	40	40	40	40	40
	Elongation, %	360	360	360	360	360	360	360
	Specific gravity	1.15	1.15	1.15	1.15	1.15	1.15	1.15
	Thickness, mm	1.4	1.4	1.4	1.4	1.4	1.4	2.1
Finished ball	Deflection under 10-130 kg loading 30 days after production (BH1), mm	3.1	2.8	2.85	2.8	2.65	2.9	2.5
	Deflection under 10-130 kg loading 350 days after measuring BH1 (BH2), mm	3	2.7	2.75	2.7	2.55	2.8	2.4
	Difference between BH1 and BH2, mm	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1
	Rebound 30 days after production (BV1), m/s	73.8	74.1	74	73.9	74.2	73.8	73.7
	Rebound 350 days after measuring BV1 (BV2), m/s	73.8	74.1	74	73.9	74.2	73.8	73.7
	Difference between BV1 and BV2, m/s	0	0	0	0	0	0	0
	Diameter, mm	42.7	42.7	42.7	42.7	42.7	42.7	42.7
	Core initial velocity - Ball initial velocity (CV - BV1)	0.5	0.6	0.6	0.6	0.7	0.5	1.2
	Core deflection/Ball deflection (CH/BH1)	1.03	1.02	1.02	1.02	0.98	1.03	1.04
	Dimples	Type	I	I	I	I	I	II
Clear coating thickness	Land areas (Y), $\mu\text{m}$	16	16	16	16	16	15	17
	Edge areas (Z), $\mu\text{m}$	14	14	14	14	14	13	8
Distance	Coating thickness ratio (Z/Y $\times$ 100), %	88	88	88	88	88	88	47
	HS 45, driver	2850	2950	2950	2950	3370	3250	3090
	Spin rate, rpm	224	226	225	224	223	222	219
	Total distance, m	221	223	222	221	220	219	212
	HS 45, driver (after abrasion test)							
	Total distance, m	-3	-3	-3	-3	-3	-3	-7
	Distance difference							
	Total distance, m							



TABLE 4-continued

			Example				Comparative Example		
			1	2	3	4	1	2	3
Durability	Durability to cracking	At incident velocity of 43 m/s	1000	1100	1100	1100	1103	1103	1575
	Abrasion test	After 144 hours of abrasion with sand	Good	Good	Good	Good	Good	Good	NG
Feel	Driver		Good	Good	Good	Good	Good	Good	Good

TABLE 5

			Comparative Example						
			4	5	6	7	8	9	10
Core	Type		No. 7	No. 8	No. 9	No. 8	No. 5	No. 5	No. 10
	Diameter, mm		39.9	39.9	39.9	39.9	39.9	39.9	42.7
	Specific gravity		1.12	1.12	1.12	1.12	1.12	1.12	1.12
	Deflection under 10-130 kg compression (CH), mm		2.75	2.75	3.8	2.75	2.6	2.6	
	Rebound (CV)		77.2	77.6	77.4	77.6	74.9	74.9	
	JIS-C hardness at core surface (A)		80	80	70	80	80	80	80
	JIS-C hardness 2 mm inside core surface (B)		75	75	65	75	75	75	75
	JIS-C hardness 5 mm inside core surface (C)		77	77	68	77	77	77	77
	JIS-C hardness 10 mm inside core surface (D)		71	71	66	71	71	71	71
	JIS-C hardness 15 mm inside core surface (E)		67	67	62	67	67	67	67
	JIS-C hardness at core center (F)		63	63	58	63	63	63	63
	JIS-C hardness difference between core surface and 5 mm inside core surface (A - C)		3	3	2	3	3	3	3
	JIS-C hardness difference between core surface and center (A - F)		17	17	12	17	17	17	17
Cover	Type		A	A	C	A	C	D	
	Shore D hardness		45	45	60	45	60	45	
	Breaking strength, MPa		40	40	17	40	17	12	
	Elongation, %		360	360	100	360	100	120	
	Specific gravity		1.15	1.15	0.99	1.15	0.99	0.99	
Finished ball	Thickness, mm		1.4	1.4	1.4	1.4	1.4	1.4	
	Deflection under 10-130 kg loading 30 days after production (BH1), mm		2.75	2.75	3.3	2.75	2.25	2.75	2.75
	Deflection under 10-130 kg loading 350 days after measuring BH1 (BH2), mm		2.5	2.5	3	2.5	2.3	2.6	2.75
	Difference between BH1 and BH2, mm		-0.25	-0.25	-0.3	-0.25	0.05	-0.15	0
	Rebound 30 days after production (BV1), m/s		76.2	76.6	77.0	76.6	74.1	73.7	74.6
	Rebound 350 days after measuring BV1 (BV2), m/s		75.7	75.8	76.6	75.8	74.2	73.8	74.7
	Difference between BV1 and BV2, m/s		-0.5	-0.8	-0.4	-0.8	0.1	0.1	0.1
	Diameter, mm		42.7	42.7	42.7	42.7	42.7	42.7	42.7
	Core initial velocity - Ball initial velocity (CV - BV1)		1.0	1.0	0.4	1.0	0.8		1.2
	Core deflection/Ball deflection (CH/BH1)		1.00	1.00	1.15	1.00	1.16		0.95
Dimples	Type		I	I	I	II	I	I	I
	Clear Land areas (Y), $\mu\text{m}$		16	16	16	17	16	16	16
	coating Edge areas (Z), $\mu\text{m}$		14	14	14	8	14	14	14
	thickness Coating thickness ratio (Z/Y $\times$ 100), %		88	88	88	47	88	88	88
	Distance HS 45, driver	Spin rate, rpm	3360	3340	3040	3340	3190	3320	3650
		Total distance, m	233	235	237	235	224	221	221
	HS 45, driver (after abrasion test)	Total distance, m	230	232	222	228	216	209	215
	Distance difference	Total distance, m	-3	-3	-15	-7	-8	-12	-6
	Durability								
	Durability to cracking	At incident velocity of 43 m/s	615	579	300	579	1350	1020	621
Feel	Abrasion test	After 144 hours of abrasion with sand	Good	Good	NG	NG	NG	NG	NG
	Driver		Good	Good	NG	Good	NG	Good	NG

[0150] The rubber material in Comparative Example 10 had a breaking strength of 15 MPa and an elongation of 88%.

[0151] In the golf ball in Comparative Example 1, the hardness profile was not optimized and the spin rate was high. As a result, the distance traveled by the ball decreased.

[0152] In the golf ball in Comparative Example 2, the hardness profile was not optimized and the spin rate was high. As a result, the distance traveled by the ball decreased.

[0153] In the golf ball in Comparative Example 3, the hardness profile was not optimized, the cover was too thick and the spin rate was high. As a result, the distance traveled by the ball decreased. In addition, the dimple edge radius of curvature R was small, as a result of which the durability to abrasion was poor and the flight performance underwent a large decrease.

[0154] In the golf ball in Comparative Example 4, zinc methacrylate was used as the co-crosslinking agent in the core formulation. As a result, the finished ball underwent large changes over time in the deflection and rebound (initial velocity), and the durability to cracking was poor.

[0155] In the golf ball in Comparative Example 5, zinc acrylate was used as the co-crosslinking agent in the core formulation. As a result, the finished ball underwent large changes over time in the deflection and rebound, and the durability to cracking was poor.

[0156] In the golf ball in Comparative Example 6, zinc acrylate was used as the co-crosslinking agent in the core formulation, in addition to which the cover had a small breaking strength and a small elongation. As a result, the finished ball underwent large changes over time in the deflection and rebound, and the durability to cracking was poor. Moreover, the cover was hard, giving the ball a poor feel on shots with a driver.

[0157] In the golf ball in Comparative Example 7, zinc acrylate was used as the co-crosslinking agent in the core formulation. As a result, the finished ball underwent large changes over time in the deflection and rebound, and the durability to cracking was poor. Moreover, the dimpled edges had a small radius of curvature R, as a result of which the finished ball had a poor durability to abrasion and exhibited a large decrease in flight performance.

[0158] In the golf ball in Comparative Example 8, the hardness profile was not optimized and the spin rate was high. As a result, the distance traveled by the ball decreased. Moreover, the cover had a small breaking strength and a small elonga-

tion, as a result of which the finished ball had a poor durability to abrasion and exhibited a large decrease in flight performance. In addition, the cover was hard, giving the ball a poor feel on shots with a driver.

[0159] In the golf ball in Comparative Example 9, the hardness profile was not optimized and the spin rate was high. As a result, the distance traveled by the ball decreased. Moreover, the cover had a small breaking strength and a small elongation, as a result of which the finished ball had a poor durability to abrasion and exhibited a large decrease in flight performance.

[0160] In the golf ball in Comparative Example 10, the surface rubber material in the one-piece construction had a small breaking strength and a small elongation, as a result of which the finished ball had a poor durability to cracking and a poor durability to abrasion, and exhibited a large decrease in flight performance.

1. A golf ball comprising a core and a cover, wherein the core is formed of a rubber composition comprising a base rubber, a co-crosslinking agent, a crosslinking initiator and a metal oxide, the base rubber being a mixture of (A) polybutadiene with (B) styrene-butadiene rubber and/or isoprene rubber, the co-crosslinking agent being methacrylic acid, the metal oxide being zinc oxide, and the rubber composition containing the crosslinking initiator in an amount of from 1.2 to 5 parts by weight per 100 parts by weight of the base rubber.

2. The golf ball of claim 1, wherein the rubber composition further includes a fatty acid metal salt.

3. The golf ball of claim 2, wherein the fatty acid metal salt is zinc stearate.

4. The golf ball of claim 2, wherein the fatty acid metal salt is included in an amount of from 0.1 to 5 parts by weight per 100 parts by weight of the base rubber.

5. The golf ball of claim 1, wherein the cover is formed of a resin material which has a breaking strength of from 20 to 80 MPa and an elongation of from 150 to 600%.

6. The golf ball of claim 1, wherein the core has a deflection (CH), when compressed under a final load of 1,275 N (130 kgf) from an initial load of 98 N (10 kgf), of from 2.0 to 7.0 mm.

7. The golf ball of claim 1, wherein the ball has an initial velocity of not more than 76 m/s.

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