



(43) International Publication Date
15 October 2015 (15.10.2015)

(10) International Publication Number
WO 2015/157066 A1

- (51) **International Patent Classification:**
C08K 5/098 (2006.01) *C08L 9/00* (2006.01)
- (21) **International Application Number:**
PCT/US2015/023896
- (22) **International Filing Date:**
1 April 2015 (01.04.2015)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
61/976,151 7 April 2014 (07.04.2014) US
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(81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) **Title:** GOLF BALL WITH RUBBER CORE, LAYER, OR BOTH AND METHOD

(57) **Abstract:** Golf ball comprising core, cover, and optional intermediate layer(s) has the core and/or intermediate layer(s) made by crosslinking a rubber composition including at least (a) 100 parts by weight polybutadiene having 85% to 100% cis-1,4 bond content; (b) about 10 to about 50 parts by weight of (i) a zinc, magnesium, or calcium salt of a first carboxylic acid with least two ethylenically unsaturated bonds and (ii) a zinc, magnesium, or calcium salt of a second carboxylic acid with one ethylenically unsaturated bond that is α,β to a carbonyl of a carboxyl group, wherein (b)(i) is about 50% by weight to 100% by weight of the combination of (b)(i) and (b)(ii); (c) a free radical initiator; and (d) an inorganic zinc, magnesium, or calcium compound. Further disclosed is a method of making this golf ball by molding and crosslinking the rubber composition to make the core or intermediate layer(s).



WO 2015/157066 A1

GOLF BALL WITH RUBBER CORE, LAYER, OR BOTH AND METHOD

[0001] The present application claims the benefit of U.S. Provisional Application

5 No. 61/976,151, filed April 7, 2014.

FIELD

[0002] The present disclosure is in the field of golf balls and relates to golf balls

10 having rubber cores, rubber layers, or both rubber cores and rubber layers and to methods of manufacturing such balls.

BACKGROUND

[0003] This section provides information helpful in understanding the disclosure but that is not necessarily prior art.

15 **[0004]** Golf balls have long featured rubber cores crosslinked with salts of acrylic or methacrylic acid, such as zinc diacrylate. However, these salts do not blend well with the uncured rubber composition (which is also called the rubber compound) of the uncrosslinked rubber polymer and curing agent such as free radical initiator and/or sulfur or sulfur compound.

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SUMMARY OF THE DISCLOSURE

[0005] This section provides a general summary of the disclosure and may not be comprehensive of its full scope or all of the disclosed features.

25 **[0006]** Disclosed is a golf ball comprising a core, a cover, and, optionally, one or more intermediate layers between the core and the cover. The core, any intermediate layer or intermediate layers or any combination thereof is made by crosslinking a rubber composition that includes at least (a) 100 parts by weight of a polybutadiene having a cis-1,4 bond content of from about 85% to 100%; (b) from about 10 to about 50 parts by weight of (i) a zinc, magnesium, or calcium salt of a first carboxylic acid having at least two
30 ethylenically unsaturated bonds and, optionally, (ii) a zinc, magnesium, or calcium salt of a second carboxylic acid having one ethylenically unsaturated bond that is α,β to a carbonyl of a carboxyl group, wherein (b)(i) is from about 50% by weight to 100% by weight of the combined weights of (b)(i) and (b)(ii); (c) a free radical initiator; and (d) an inorganic zinc, magnesium, or calcium compound. Further disclosed is a method of making this golf ball by

molding and crosslinking the rubber composition to make the golf ball core and/or one or more intermediate layers. Further disclosed is the golf ball just described in which (b)(i) is from about 50% by weight to about 99% by weight of the combination of (b)(i) and (b)(ii).

[0007] The core is the central sphere of the golf ball, while the cover is the

5 outermost structural layer of the golf ball. Coating layers (whether paint layers or clear coating layers) are not considered to be structural layers.

[0008] The disclosed golf ball and the golf ball made by the disclosed method of manufacture can each comprise a first carboxylic acid comprising at least two conjugated, ethylenically unsaturated bonds. The conjugated, ethylenically unsaturated bonds may

10 further be conjugated with a carbonyl group.

[0009] The disclosed golf ball and the golf ball made by the disclosed method of manufacture can each comprise a first carboxylic acid in which at least one of the ethylenically unsaturated bonds is conjugated with a carbonyl group.

[0010] In another example of the disclosed golf ball and golf ball made by the

15 disclosed method, the first carboxylic acid, or the second carboxylic acid or both can be a monocarboxylic acid.

[0011] The first carboxylic acid can comprise a linear carboxylic acid, such as a linear carboxylic acid having at least 6 carbon atoms. The first carboxylic acid can comprise sorbic acid.

[0012] The salt of the first carboxylic acid can comprise or consist of a zinc salt. The zinc salt of the first carboxylic acid can comprise or consist of a zinc salt of a linear carboxylic acid. The zinc salt of the first carboxylic acid can comprise or consist of a zinc salt of a linear carboxylic acid having at least 6 carbon atoms. The zinc salt of the first carboxylic acid can comprise or consist of zinc disorbate. In one example, the rubber

20 composition can further comprise zinc stearate. In yet another example, the inorganic zinc, magnesium or calcium compound can comprise zinc oxide, and the rubber composition can further comprise zinc stearate.

[0013] The second carboxylic acid can comprise acrylic acid, methacrylic acid, or a combination thereof. The second carboxylic acid can comprise or consist of acrylic acid. The second carboxylic acid can comprise or consist of methacrylic acid. The salt of the second carboxylic acid can comprise a zinc salt. The zinc salt of the second carboxylic acid can comprise or consist of zinc diacrylate. The zinc salt of the second carboxylic acid can comprise or consist of zinc dimethacrylate. In one example, the rubber composition can further include zinc stearate. In yet another example, the inorganic zinc, magnesium or

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calcium compound can comprise zinc oxide, and the rubber composition can further comprise zinc stearate.

[0014] The rubber composition can comprise from about 25 to about 40 parts by weight of (b)(i). When salt (b)(i) and optional salt (b)(ii) are both present in the rubber composition, the concentration of (b)(i) can be from about 50% by weight to about 99% by weight of the combination of (b)(i) and (b)(ii), or from about 50% by weight to about 90% by weight of the combination of (b)(i) and (b)(ii), or from about 60% by weight to about 75% by weight of the combination of (b)(i) and (b)(ii). The polybutadiene of the rubber compound can have a cis-1,4 bond content of from about 95% to about 100% or from 95% to about 99% or from 95% to about 98%.

[0015] In certain examples, the free radical initiator of the rubber compound can comprise a member selected from the group consisting of dialkyl peroxides, alkyl hydroperoxides, diacyl peroxides, peroxyketals, peroxyesters and any combination thereof. The rubber composition in certain examples comprises from about 0.05 to about 3 parts by weight of the free radical initiator (c) based on 100 parts by weight of polybutadiene (a).

[0016] In certain embodiments, the golf ball has an intermediate layer formed of the rubber composition and a core can formed from a composition comprising a combination of (e) a copolymer of an alpha-olefin, an α,β -ethylenically unsaturated carboxylic acid, and optionally a softening comonomer and (f) a monocarboxylic acid that is neutralized at least about 80% and up to 100% on a molar basis by a metal cation. The combination of (e) and (f) can be neutralized to a level of from about 80% to about 100% on a molar basis by metal cations. The metal cations can be zinc, magnesium or calcium cations. The metal cations can comprise or consist of zinc cations.

[0017] Also disclosed is a golf ball comprising a core, a cover, and, optionally, one or more intermediate layers between the core and the cover in which The core, any intermediate layer or intermediate layers, or any combination thereof is made by crosslinking a rubber composition that includes at least (a) 100 parts by weight of a polybutadiene having a cis-1,4 bond content of about 85% to 100%; (b) from about 10 to about 50 parts by weight of (i) a zinc salt of a first carboxylic acid that has at least two ethylenically unsaturated bonds and, optionally, (ii) a zinc salt of a second carboxylic acid that has one ethylenically unsaturated bond that is α,β to a carbonyl of a carboxyl group, wherein (b)(i) is from about 50% by weight to 100% by weight of the combination of (b)(i) and (b)(ii); (c) a free radical initiator; and (d) an inorganic zinc compound. Further disclosed is the golf ball just described in which (b)(i) is from about 50% by weight to about 99% by

weight of the combination of (b)(i) and (b)(ii). Still further disclosed is a method of making this golf ball by molding and crosslinking the rubber composition to make the golf ball core and/or one or more intermediate layers. Cis-1,4 bond content is given as a percentage of monomer units making up the polybutadiene.

5 **[0018]** Also disclosed are golf balls and methods of making them in which the core, any intermediate layer or intermediate layers, or any combination thereof is made by crosslinking the above butadiene rubber composition made with a zinc, magnesium, or calcium salt of a first carboxylic acid having at least two ethylenically unsaturated bonds (i) in which at least two of the ethylenically unsaturated bonds are conjugated. In one example,
10 the salt of the first carboxylic acid is a zinc salt.

[0019] Also disclosed are golf balls and methods of making them in which the core, any intermediate layer or intermediate layers, or any combination thereof is made by crosslinking the above butadiene rubber composition made with a zinc, magnesium, or calcium salt of a first carboxylic acid having at least two ethylenically unsaturated bonds (i)
15 in which one of the ethylenically unsaturated bonds is conjugated with a carbonyl group.

[0020] Also disclosed are golf balls and methods of making them in which the core, any intermediate layer or intermediate layers, or any combination thereof is made by crosslinking the above butadiene rubber composition in which a carboxylic acid used for one of the first and second carboxylic acids is a monocarboxylic acid or both are monocarboxylic
20 acids. In various examples, both salt (i) and salt (ii) are or include zinc salts.

[0021] Also disclosed are golf balls and methods of making them in which the core, any intermediate layer or intermediate layers, or any combination thereof is made by crosslinking the above butadiene rubber composition in which the zinc, magnesium, or calcium salt (i) includes or is zinc disorbate, the zinc, magnesium, or calcium salt (ii) includes
25 or is zinc diacrylate, or both the zinc, magnesium, or calcium salt (i) includes or is zinc disorbate and the zinc, magnesium, or calcium salt (ii) includes or is zinc diacrylate. Further disclosed are these golf balls and methods of making them in which the butadiene rubber composition further includes zinc stearate.

[0022] An “ethylenically unsaturated bond” is a carbon-to-carbon double bond.
30 “A,” “an,” “the,” “at least one,” and “one or more” are used interchangeably to indicate that at least one of the item is present; a plurality of such items may be present unless the context clearly indicates otherwise. All numerical values of parameters (e.g., of quantities or conditions) in this specification, including the appended claims, are to be understood as being modified in all instances by the term “about” whether or not “about” actually appears before

the numerical value. "About" indicates that the stated numerical value allows some slight imprecision (with some approach to exactness in the value; approximately or reasonably close to the value; nearly). If the imprecision provided by "about" is not otherwise understood in the art with this ordinary meaning, then "about" as used herein indicates at least variations that may arise from ordinary methods of measuring and using such parameters. In addition, disclosure of ranges includes disclosure of all values and further divided ranges within the entire range. Each value within a range and the endpoints of a range are hereby all disclosed as separate embodiment. The ranges set forth herein include their endpoints unless expressly stated otherwise. When an amount, concentration, or other value or parameter is given as a range, one or more preferred ranges or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether such pairs are separately disclosed. The scope of the invention is not limited to the specific values recited when defining a range. In this description of the invention, for convenience, "polymer" and "resin" are used interchangeably to encompass resins, oligomers, and polymers. The terms "comprises," "comprising," "including," and "having," are inclusive and therefore specify the presence of stated items, but do not preclude the presence of other items. As used in this specification, the term "or" means any of the listed items individually or in any and all combinations with one or more of the other listed items. Further, as used herein, the terminology "at least" is equivalent to "greater than or equal to," and the terminology "up to" is equivalent to "less than or equal to."

[0023] It should be understood that the description and specific examples are intended for purposes of illustration only and are not intended to limit the scope of the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] The drawings illustrate some aspects of the disclosed technology.

[0025] The FIG. is a schematic, cross-sectional view of a golf ball.

[0026] The parts of the figure are not necessarily to scale.

DETAILED DESCRIPTION

[0027] A detailed description including exemplary, nonlimiting embodiments follows.

[0028]

The rubber composition used to make the golf ball includes at least (a) 100 parts by weight of a polybutadiene having a cis-1,4 bond content of from about 85% to 100%; (b) from about 10 to about 50 parts by weight of (i) a zinc, magnesium, or calcium salt of a first carboxylic acid having at least two ethylenically unsaturated bonds and, optionally,
 5 (ii) a zinc, magnesium, or calcium salt of a second carboxylic acid having one ethylenically unsaturated bond α,β to a carbonyl of a carboxyl group, wherein (b)(i) is from about 50% by weight to 100% by weight of the combination of (b)(i) and (b)(ii); (c) a free radical initiator; and (d) an inorganic zinc, magnesium, or calcium compound. The rubber composition is molded and cured to form core, an intermediate layer, a plurality of intermediate layers, or
 10 any combination of these of the golf ball.

[0029]

The polybutadiene has a cis-1,4 bond content of from about 85%, or from about 90%, or from about 95%, or from about 98% up to 100%. In addition, the polybutadiene can have a 1,2-vinyl bond content of 0% up to about 2%, or 0 up to about 1.7%, or 0% up to about 1.5%. Useful polybutadiene polymers include those having a
 15 Mooney viscosity (ML1+4 (100° C.)) between 20 and 80, or from 35 to 65 (test method ASTM D1646). In various embodiments, a polybutadiene having a weight-average molecular weight (Mw) of 450,000 to 850,000 and a polydispersity (weight-average molecular weight (Mw) to number-average molecular weight (Mn) ratio) of 5 or less is used. Molecular weights can be determined by gel permeation chromatograph using polystyrene
 20 standards.

[0030]

Although the catalyst used for synthesizing the polybutadiene is not subject to any specific limitation, the polybutadiene can be synthesized using a catalyst of a group VIII element such as nickel or cobalt or a catalyst of rare-earth element such as neodymium. Exemplary rare-earth catalysts include those made up of a combination of a
 25 lanthanide series rare-earth compound, an organoaluminum compound, an alumoxane, a halogen-bearing compound, and an optional Lewis base. Examples of suitable lanthanide series rare-earth compounds include halides, carboxylates, alcoholates, thioalcoholates and amides of atomic number 57 to 71 metals. Organoaluminum compounds that may be used include those of the formula $\text{AlR}^1\text{R}^2\text{R}^3$ (wherein R^1 , R^2 , and R^3 are each independently a
 30 hydrogen or a hydrocarbon group of 1 to 8 carbons). Preferred alumoxanes include linear compounds of the structure $\text{R}^4\text{AlR}^4(\text{OAlR}^4)_n\text{R}^4$ or cyclic compounds



in which R^4 is a hydrocarbon group having 1 to 20 carbon atoms and n is an integer greater than or equal to 3. Examples of halogen-bearing compounds that may be used include aluminum halides of the formula AlX_nR_{3-n} (wherein X is a halogen; R is a hydrocarbon group of 1 to 20 carbons, such as an alkyl, aryl or aralkyl; and n is 1, 1.5, 2 or 3); strontium halides such as Me_3SrCl , Me_2SrCl_2 , $MeSrHCl_2$ and $MeSrCl_3$; and other metal halides such as silicon tetrachloride, tin tetrachloride and titanium tetrachloride. The Lewis base can be used to form a complex with the lanthanide series rare-earth compound. Illustrative examples include acetylacetone and ketone alcohols. It is particularly preferred to use a neodymium compound as the lanthanide series rare-earth compound.

10 **[0031]** The polymerization of butadiene in the presence of a rare-earth catalyst may be carried out by bulk polymerization or vapor phase polymerization, either with or without the use of solvent, and at a polymerization temperature that can be in a range of from -30 to $+150^\circ C$. or from 10 to $100^\circ C$.

15 **[0032]** The polybutadiene should be included in the rubber composition in an amount of at least about 50 wt %, or at least about 60 wt %, or at least about 65 wt %, and up to about 90 wt %, or up to 80 wt %, or up to 70 wt %. In general, the polybutadiene may be from about 50 wt % to about 90 wt %, or from about 65 wt % to about 70 wt % of the rubber composition.

20 **[0033]** Other rubber polymers may be combined with the polybutadiene, for example in amounts of 0-10 wt%, based on total rubber polymer including the polybutadiene. Nonlimiting examples of suitable other rubber polymers include styrene-butadiene rubbers (SBR), natural rubbers, polyisoprene rubbers, and ethylene-propylene-diene rubbers (EPDM), which may be used singly or as combinations of two or more. In a preferred embodiment, the polybutadiene having a cis-1,4 bond content of at least about 85% is the only rubber polymer
25 used.

30 **[0034]** Based on 100 parts by weight of the polybutadiene rubber having a cis-1,4 bond content of from about 85% to 100%, the rubber composition includes from about 10 to about 50 parts by weight of (b)(i) a zinc, magnesium, or calcium salt of a carboxylic acid having at least two ethylenically unsaturated bonds and (b)(ii) a zinc, magnesium, or calcium salt a carboxylic acid having one ethylenically unsaturated bond α,β to a carbonyl of a carboxyl group. The zinc, magnesium, or calcium salt of a carboxylic acid having at least two ethylenically unsaturated bonds (b)(i) is from about 50% by weight to 100% by weight of the combination of zinc, magnesium, or calcium salts (b)(i) and (b)(ii).

[0035] The carboxylic acid having at least two ethylenically unsaturated bonds making zinc, magnesium, or calcium salt (b)(i) can be a zinc salt.

[0036] The carboxylic acid having at least two ethylenically unsaturated bonds making the zinc, magnesium, or calcium salt (b)(i) can be a monocarboxylic acid or a dicarboxylic acid, or can be a monocarboxylic acid. In certain embodiments, two or more of the ethylenically unsaturated bonds of the zinc, magnesium, or calcium salt of a carboxylic acid (b)(i) are conjugated. In these or other embodiments, one of the ethylenically unsaturated bonds is conjugated with a carbonyl group.

[0037] Additionally, the zinc, magnesium, or calcium salt of a carboxylic acid having at least two ethylenically unsaturated bonds (b)(i) can be a zinc, magnesium, or calcium salt of a linear carboxylic acid having at least 6 carbon atoms.

[0038] Nonlimiting examples of suitable zinc, magnesium, and calcium salts of carboxylic acids having at least two ethylenically unsaturated bonds (b)(i) include zinc, magnesium, and calcium salts of carboxylic acids selected from sorbic acid, 2,4-pentadienoic acid, 2,6-heptadienoic acid, 5,7-octadienoic acid, 3,7-dimethyl-2,6-octadienoic acid (geranic acid), 2,6-octadienedioic acid, 2,4-nonadienoic acid, 2,6-nonadienoic acid, 2,4-decadienoic acid, muconic acid (hexa-2,4-dienedioic acid), linoleic acid (9,12-octadecadienoic acid), 5,8,11,14-eicosatetraenoic acid (arachidonic acid), calendic acid, catalpic acid, eicosapentaenoic acid, rumenic acid, docosahexaenoic acid, 6,9,12-octadecatrienoic acid (γ -linolenic acid), 8,11,14-eicosatrienoic acid (dihomo- γ -linolenic acid), 7,10,13,16-docosatetraenoic acid, 4,7,10,13,16-docosapentaenoic acid, 9,12,15-octadecatrienoic acid (α -linolenic acid), 6,9,12,15-octadecatetraenoic acid (stearidonic acid), 8,11,14,17-eicosatetraenoic acid, 5,8,11,14,17-eicosapentaenoic acid, 7,10,13,16,19-docosapentaenoic acid, 4,7,10,13,16,19-docosahexaenoic acid, 6,9,12,15,18,21-tetracosenoic acid (nisinic acid), 5,8,11-eicosatrienoic acid, α -eleostearic acid, jacaric acid, punicic acid, rumelenic acid, parinaric acid, taxoleic acid, pinolenic acid, sciadonic acid, monoesters of any of the mentioned dicarboxylic acids (e.g., C_1 to C_{18} alkyl esters such as the methyl ester of muconic acid or the ethyl ester of 2,6-octadienedioic acid), halo, alkyl, or aryl substituted derivatives of these, and combinations of these. Preferred among these are zinc salts of sorbic acid and its halo, alkyl, or aryl substituted derivatives, and combinations of these. Particularly preferred as the zinc, magnesium, or calcium salt of a carboxylic acid having at least two ethylenically unsaturated bonds (b)(i) is the zinc salt of sorbic acid (zinc disorbate).

[0039] In certain examples, the zinc, magnesium, or calcium salt of a carboxylic acid having at least two ethylenically unsaturated bonds (b)(i) can be from about

20 to about 40 parts by weight, or from about 20 to about 28 parts by weight, based on 100 parts by weight of the polybutadiene.

[0040]

The zinc, magnesium, or calcium salt of a carboxylic acid having one ethylenically unsaturated bond that is α,β to a carbonyl of a carboxyl group (b)(ii) can be a zinc, magnesium, or calcium salt of monocarboxylic acid or a dicarboxylic acid, or can be a monocarboxylic acid. Nonlimiting examples of suitable zinc, magnesium, and calcium salts of carboxylic acids having one ethylenically unsaturated bond α,β to a carbonyl of a carboxyl group (b)(ii) include zinc, magnesium, and calcium salts of carboxylic acids selected from acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid, and combinations of these. The zinc, magnesium, or calcium salt of a carboxylic acid having one ethylenically unsaturated bond α,β to a carbonyl of a carboxyl group (b)(ii) can be at least one of zinc diacrylate and zinc dimethacrylate or can be zinc diacrylate.

[0041]

The zinc, magnesium, or calcium salt of a carboxylic acid having at least two ethylenically unsaturated bonds (b)(i) is at least about 50%, or at least about 55% by weight, or at least about 60% by weight, or at least about 65% by weight and up to 100% by weight, or up to 99% by weight, or up to 95% by weight, or up to about 90% by weight or up to about 85% by weight or up to about 80% by weight, or up to about 75% by weight of the combined weights of the ethylenically unsaturated acid zinc, magnesium, or calcium salts (b)(i) and (b)(ii) in the rubber composition. The zinc, magnesium, or calcium salt of a carboxylic acid having at least two ethylenically unsaturated bonds (b)(i) may be from about 50% by weight to about 100% by weight, and example ranges of the preferred upper and lower limits given may be from about 50% by weight to about 99% by weight, or from about 50% by weight to about 90% by weight, or from about 65% by weight to about 85% by weight, or from about 65% by weight to about 75% by weight of the combination of the ethylenically unsaturated acid zinc, magnesium, or calcium salts (b)(i) and (b)(ii).

[0042]

Based on 100 parts by weight of the polybutadiene rubber having a cis-1,4 bond content of about 85% to 100%, the zinc, magnesium, or calcium salts (b)(i) and (b)(ii), which may both be zinc salts, are included in the rubber composition in a combined amount of from about 10 to about 50 parts by weight, or in a combined amount in a range with a lower limit of about 12 or about 15 or about 20 parts by weight and an upper limit of about 45 or about 40 or about 35 or about 30 parts by weight. Specific ranges that may be mentioned for the combined content of zinc, magnesium, or calcium salts (b)(i) and (b)(ii) in the rubber composition are from about 15 to about 45 or from about 20 to about 35 or from

about 20 to about 30 parts by weight based on 100 parts by weight of the polybutadiene having a cis-1,4 bond content of about 85% to 100%.

[0043] The rubber composition further includes a free radical initiator in an amount effective to crosslink the rubber composition to a desired extent during molding and curing (crosslinking, also called vulcanizing) of the core or intermediate layer or layers made from the rubber composition.

[0044] Suitable organic peroxides may include, but are not limited to, dialkyl peroxides, alkyl hydroperoxides, diacyl peroxides, acyl hydroperoxides peroxyketals, peroxyesters, peroxydicarbonates, and peroxy monocarbonates. In certain embodiments, the organic peroxides include dialkyl peroxides, alkyl hydroperoxides, diacyl peroxides, acyl hydroperoxides, peroxyketals, peroxyesters, and combinations of these. Nonlimiting examples of suitable organic peroxides include, but are not limited to, di-*t*-amyl peroxide; di-*t*-butyl peroxide; *t*-butyl cumyl peroxide; dicumyl peroxide; *t*-butyl hydroperoxide, cumene hydroperoxide, diisopropylbenzene hydroperoxide di(2-methyl-1-phenyl-2-propyl) peroxide; *t*-butyl-2-methyl-1-phenyl-2-propyl peroxide; di(*t*-butylperoxy)-diisopropylbenzene; benzoyl peroxide; 1,1-di(*t*-butoxy)-3,3,5-trimethyl cyclohexane; 1,1-di(*t*-hexylperoxy)-3,3,5-trimethylcyclohexane; 1,1-di(*t*-butylperoxy)-2-methylcyclohexane; 3,3,5,7,7-pentamethyl-1,2,4-trioxepane; cumyl hydroperoxide; *t*-butyl hydroperoxide; 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexane; 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexyne; 2,5-dimethyl-2,5-di(benzoylperoxy)hexane; 2,2'-bis(*t*-butylperoxy)-di-*iso*-propylbenzene; *n*-butyl 4,4-bis(*t*-butylperoxy)valerate; *t*-butyl perbenzoate; benzoyl peroxide; 1,1-di(*t*-hexylperoxy)cyclohexane, 1,1-di(*t*-butylperoxy)cyclohexane, 2,2-di[4,4-di(*t*-butylperoxy)cyclohexane]propane, 2,2-di(*t*-butylperoxy)butane; *n*-butyl 4,4'-bis(butylperoxy)valerate; *t*-amyl perbenzoate; α,α -bis(*t*-butylperoxy)diisopropylbenzene; and combinations thereof. Suitable azo compounds may include, but are not limited to, azobisisobutyronitrile (AIBN); 1,1'-azobis(cyclohexanecarbonitrile) (ABCN); 2,2'-azodi(2-methylbutyronitrile) (AMBN); 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride; 2,2'-azobis[2-(2-imidazolin-2-yl)propane]disulfate dehydrate; 2,2'-azobis(2-methylpropionamidine)dihydrochloride; 2,2'-azobis[N-(2-carboxyethyl)-2-methylpropionamidine]hydrate; 2,2'-azobis{2-[1-(2-hydroxyethyl)-2-imidazolin-2-yl]propane}dihydrochloride; 2,2'-azobis[2-(2-imidazolin-2-yl)propane]; 2,2'-azobis(1-imino-1-pyrrolidino-2-ethylpropane)dihydrochloride; 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide}; 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide]; and combinations thereof.

[0045] The free radical initiator may be used in an amount of from about 0.05 to about 3 parts by weight based on 100 parts by weight of polybutadiene.

[0046] It is also possible to include an organosulfur compound in the base rubber so as to confer a good rebound. Here, it is recommended that thiophenols, thionaphthols, halogenated thiophenols, or metal salts thereof be included as the organosulfur compound. Illustrative examples include pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol, the zinc salt of pentachlorothiophenol, and diphenylpolysulfides, dibenzylpolysulfides, dibenzoylpolysulfides, dibenzothiazoylpolysulfides and dithiobenzoylpolysulfides having from 2 to 4 sulfurs. The use of diphenyldisulfide or the zinc salt pentachlorothiophenol is especially preferred.

[0047] The organosulfur compound may be included in an amount, per 100 parts by weight of the polybutadiene, of at least 0.05 part by weight, or at least 0.1 part by weight, or at least 0.15 part by weight in an amount generally not more than 5 parts by weight, or not more than 3 parts by weight, or not more than 2.5 parts by weight. Including organosulfur compound in an amount within the disclosed ranges can improve rebound (coefficient of restitution), but exceeding the upper limit may detrimentally affect the feel on impact without further increasing rebound.

[0048] The rubber composition further includes an inorganic zinc, magnesium, or calcium compound. Nonlimiting examples of inorganic zinc, magnesium, and calcium compounds that may be used include zinc oxide, magnesium oxide, calcium carbonate, magnesium carbonate, zinc sulfide, calcium metasilicate, and the like. The inorganic zinc, magnesium, or calcium compound is used in an amount sufficient to keep the carboxylic acids in their salts forms. In general, the inorganic zinc, magnesium, or calcium compound is included in the rubber composition in an amount of at least about 4 parts by weight based on 100 parts by weight polybutadiene and may be included in greater amounts as a filler, for example up to about 30 parts by weight based on 100 parts by weight polybutadiene. Inorganic zinc compounds are particularly preferred.

[0049] The polybutadiene rubber composition may include a filler in addition to the inorganic zinc compound such as, but not limited to, clay, talc, asbestos, graphite, glass, mica, barium sulfate, aluminum hydroxide, silicates, diatomaceous earth, carbonates, metals (such as titanium, tungsten, zinc, aluminum, bismuth, nickel, molybdenum, iron, copper, brass, boron, bronze, cobalt, beryllium, and alloys of these), metal oxides (such as iron oxide, aluminum oxide, titanium oxide, zirconium oxide and the like), particulate synthetic plastics (such as high molecular weight polyethylene, polypropylene, polystyrene,

polyethylene ionomeric resins, polyamide, polyester, polyurethane, polyimide, and the like), particulate carbonaceous materials (such as carbon black, and the like), as well as cotton flock, cellulose flock, cellulose pulp, leather fiber, and combinations of any of the above.

Non-limiting examples of heavy-weight filler components that may be used to increase the specific gravity of the cured elastomer may include titanium, tungsten, aluminum, bismuth, nickel, molybdenum, iron, steel, lead, copper, brass, boron, boron carbide whiskers, bronze, cobalt, beryllium, zinc, tin, metal oxides (such as iron oxide, aluminum oxide, titanium oxide, and zirconium oxide), metal sulfates (such as barium sulfate), metal carbonates, and combinations thereof. Non-limiting examples of light-weight filler components that may be used to decrease the specific gravity of the cured elastomer may include particulate plastics, hollow glass spheres, ceramics, and hollow spheres, regrinds, or foams thereof.

[0050] The amount of inorganic filler included in the rubber composition, based on 100 parts by weight of the polybutadiene, including the inorganic zinc compound, may range from about 4 to about 30 parts by weight, or from about 5 to about 25 parts by weight, or from about 10 to about 20 parts by weight.

[0051] The polybutadiene rubber composition may include one or more various other additives, including processing agents, antioxidants, pigments, plasticizers, nano-clays, nano-carbon, graphite, nano-silica, and the like, and combinations thereof.

[0052] Among such additives that may be included are zinc, magnesium, or calcium salts of saturated or monoethylenically unsaturated fatty acids, for example zinc, magnesium, or calcium salts of such fatty acids having at least 14 carbon atoms, for example fatty acids having 14 to 18 carbon atoms, including zinc salts of these fatty acids, such as zinc stearate, zinc laurate, zinc palmitate, and the like. The zinc, magnesium, or calcium salts of saturated or monoethylenically unsaturated fatty acids may be used in amounts of from about 0 to about 15 parts by weight, or from about 0 to about 5 parts by weight or about 1 to about 15 parts by weight or about 1 to about 5 parts by weight, based on 100 parts by weight of the polybutadiene.

[0053] A monophenol-type antioxidant is a preferred antioxidant. The monophenol-type antioxidant may be included in an amount, per 100 parts by weight of the polybutadiene, of preferably from 0.01 to 0.4 part by weight, more preferably from 0.05 to 0.3 part by weight, and even more preferably from 0.1 to 0.2 part by weight. Illustrative examples of the monophenol-type antioxidant include 2,6-di-t-butyl-4-methylphenol, 2,6-di-t-butyl-4-ethylphenol, mono(α -methylbenzyl)phenol, di(α -methylbenzyl)phenol, tri(α -methylbenzyl)phenol, 2-t-butyl-4-methoxyphenol, 3-t-butyl-4-methoxyphenol, and stearyl- β -

(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate. The use of 2,6-di-*t*-butyl-4-methylphenol is especially preferred.

[0054]

As shown in the Figure, a golf ball 10 includes a core 12, a cover 18 that forms an outermost layer of golf ball 10, and intermediate layers 14, 16. At least one of the core 12, intermediate layer 14 or intermediate layer 16 is prepared by molding and crosslinking the disclosed rubber composition. While the Figure generally illustrates a ball 10 with a four-piece construction, the disclosed technology may be used to prepare a two-piece ball with a rubber core and a cover, a three-piece ball with a core, an intermediate layer, and a cover in which at least one of the core and the intermediate layer is prepared from the rubber composition, as well as balls with five or more pieces. In general, the cover 18 defines an outermost layer of the ball 10 and includes any desired number of dimples including, for example, between 280 and 432 total dimples, and in some examples, between 300 and 392 total dimples, and typically between 298 to 360 total dimples. As known in the art, the inclusion of dimples generally decreases the aerodynamic drag of the ball, which may provide for greater flight distances when the ball is properly struck. In golf ball 10, each layer (including the center 12, cover 18, and intermediate layers 14, 16) is substantially concentric with every other layer such that every layer shares a common geometric center.

[0055]

The polybutadiene composition is molded and crosslinked to form the golf ball core (for example core 12 of the four-piece ball illustrated in the Figure), intermediate layer (for example, intermediate layer 14 or 16 of the four-piece ball illustrated in the Figure), a plurality of intermediate layers, or any combination of these of the golf ball, for example by compression molding at temperatures of from about 100 to about 200 °C for about 10 to 40 minutes. When the polybutadiene composition is used to form an intermediate layer, the polybutadiene composition may first be pre-molded into two hemispherical shells, optionally with partial crosslinking, that are then, for example, compression molded about the core or the core with one or more already-formed intermediate layers about it.

[0056]

The crosslinking or vulcanization temperature for the core can be at least 150° C., or at least 155° C., but generally not more than 200° C., or not more than 190° C., or not more than 180° C., or not more than 170° C.

[0057]

The components of the golf ball—core, intermediate layer or layers, and cover—not made from the polybutadiene rubber composition may be made from suitable thermoplastic elastomers, for example metal cation ionomers of addition copolymers, metallocene-catalyzed block copolymers of ethylene and α -olefins having 4 to about 8 carbon atoms, thermoplastic polyamide elastomers (PEBA or polyether block polyamides),

thermoplastic polyester elastomers, thermoplastic styrene block copolymer elastomers such as poly(styrene-butadiene-styrene), poly(styrene-ethylene-*co*-butylene-styrene), and poly(styrene-isoprene-styrene), thermoplastic polyurethane elastomers, thermoplastic polyurea elastomers, and dynamic vulcanizates of rubbers in these thermoplastic elastomers and in other thermoplastic matrix polymers.

[0058] One preferred golf ball is made with a core including an ionomer resin or highly neutralized polymer and an intermediate layer, for example adjacent the core, made by crosslinking the disclosed butadiene rubber composition comprising 100 parts by weight of a polybutadiene having a *cis*-1,4 bond content of at least 40%, from 10 to 40 parts by weight of zinc disorbate, and at least one free radical initiator, a cover, and, optionally, one or more further intermediate layers.

[0059] Ionomer resins are metal cation ionomers of addition copolymers of alpha-olefin, for example ethylene, copolymers with an α,β -ethylenically unsaturated carboxylic acids, for example C_3 to C_8 α,β -ethylenically unsaturated carboxylic acids, such as acrylic or methacrylic acid. The copolymers may also contain a softening monomer such as an alkyl acrylate or methacrylate, for example a C_1 to C_8 alkyl acrylate or methacrylate ester or vinyl acetate. "Softening" means that the inclusion of the comonomer lowers the crystallinity of the terpolymer compared to that of an acid-only dipolymer.

[0060] The weight percentage of α,β -ethylenically unsaturated carboxylic acid monomer units in the ionomer copolymer may be in a range having a lower limit of about 1 or about 2 or about 4 or about 6 or about 8 or about 10 or about 12 or about 15 or about 20 weight percent and an upper limit of about 20 (when the lower limit is not 20) or about 25 or about 30 or about 35 or about 40 weight percent based on the total weight of the acid copolymer. The α,β -ethylenically unsaturated acid can be selected from acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, crotonic acid, fumaric acid, itaconic acid, and combinations of these. In various embodiments, acrylic acid and methacrylic acid may be used as the α,β -ethylenically unsaturated acid.

[0061] The acid monomer can be copolymerized with an alpha-olefin selected from ethylene and propylene. The weight percentage of alpha-olefin units in the ionomer copolymer may be at least about 15 or about 20 or about 25 or about 30 or about 40 or about 50 or about 60 weight based on the total weight of the acid copolymer.

[0062] Nonlimiting examples of suitable softening comonomers are alkyl esters of C_{3-8} α,β -ethylenically unsaturated carboxylic acids, particularly those in which the alkyl group has 1 to 8 carbon atoms, for instance methyl methacrylate, ethyl acrylate, ethyl

methacrylate, propyl acrylate, propyl methacrylate, butyl acrylate, butyl methacrylate, isobutyl acrylate, tert-butyl methacrylate, hexyl acrylate, 2-ethylhexyl methacrylate, and combinations of these. When the ionomer includes a softening comonomer, the softening comonomer monomer units may be present in a weight percentage of the copolymer in a range with a lower limit of a finite amount more than zero, or about 1 or about 3 or about 5 or about 11 or about 15 or about 20 weight percent of the copolymer and an upper limit of about 23 or about 25 or about 30 or about 35 or about 50 weight percent of the copolymer. The softening monomer, when present, can be present in a finite amount, such as at least about 3 weight percent or at least about 5 weight percent or at least about 10 weight percent, up to about 23 weight percent or up to about 25 weight percent or up to about 30 or up to about 45 or up to about 50 weight percent, or from about 3 weight percent to about 50 weight percent, of the copolymer.

[0063]

Nonlimiting specific examples of acid-containing ethylene copolymers include copolymers of ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/n-butyl acrylate, ethylene/methacrylic acid/isobutyl acrylate, ethylene/acrylic acid/isobutyl acrylate, ethylene/methacrylic acid/n-butyl methacrylate, ethylene/(meth)acrylic acid/hexyl (meth)acrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacrylate. Preferred acid-containing ethylene copolymers include copolymers of ethylene/methacrylic acid/n-butyl acrylate, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/acrylic acid/ethyl acrylate, ethylene/methacrylic acid/ethyl acrylate, and ethylene/acrylic acid/methyl acrylate. In various embodiments the most preferred acid-containing ethylene copolymers include ethylene/(meth)acrylic acid/n-butyl acrylate, ethylene/(meth)acrylic acid/ethyl acrylate, and ethylene/(meth)acrylic acid/methyl acrylate copolymers. The term “(meth)acrylate” is used to mean methacrylate or acrylate; the term “(meth)acrylic” is used to mean acrylic or methacrylic.

[0064]

A highly neutralized polymer is prepared by combining a metal cation ionomers of a copolymer of an alpha-olefin, such as ethylene, an α,β -ethylenically unsaturated carboxylic acid, such as C_3 to C_8 α,β -ethylenically unsaturated carboxylic acids, particularly acrylic or methacrylic acid and optionally a softening comonomer, with a sufficiently high molecular weight, mono-functional carboxylic acid or salt thereof to the acid copolymer or ionomer so that the acid copolymer or ionomer can be neutralized, without losing processability, to a level above the level that would cause the ionomer alone to become

non-melt-processable. The monomeric, mono-functional organic acid its salt may be added to the ethylene-unsaturated acid copolymers before they are neutralized or after they are optionally partially neutralized to a level between about 1 and about 100%, provided that the level of neutralization is such that the resulting ionomer remains melt-processable. In

5 generally, when the monomeric, mono-functional organic acid is included the acid groups of the copolymer may be neutralized from at least about 80% to 100%, or at least about 90% to about 100%, or at least about 95% to about 100%, or about 100% without losing processability. Such high neutralization, particularly to levels of at least about 80% or at least about 90% or at least about 95% or about 100%, without loss of processability can be
10 done by (a) melt-blending the ethylene α,β -ethylenically unsaturated carboxylic acid copolymer or a melt-processable salt of the copolymer with the organic acid or the salt of the organic acid, and (b) adding a sufficient amount of a cation source up to 110% of the amount needed to neutralize the total acid in the copolymer or ionomer and organic acid or salt to the desired level to increase the level of neutralization of all the acid moieties in the mixture or at
15 least about 80%, at least about 90%, at least about 95%, or to about 100%. To obtain 100% neutralization, it is preferred to add a slight excess of up to 110% of cation source over the amount stoichiometrically required to obtain the 100% neutralization can be added.

[0065] The neutralizing cation used may be any metal cation. Suitable cations include lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, aluminum,
20 bismuth, chromium, cobalt, copper, strontium, titanium, tungsten, or a combination of these cations; in various embodiments alkali, alkaline earth, or zinc metal cations are preferred.

[0066] The preferred monomeric, monofunctional organic acids are aliphatic or aromatic saturated or unsaturated acids that may have from 6 or about 8 or about 12 or about 18 carbon atoms to about 36 carbon atoms or less than 36 carbon atoms. Nonlimiting
25 suitable examples of the monomeric, monofunctional organic acid includes caproic acid, caprylic acid, capric acid, lauric acid, stearic acid, behenic acid, erucic acid, oleic acid, linoleic acid, myristic acid, benzoic acid, palmitic acid, phenylacetic acid, naphthalenoic acid, dimerized derivatives of these, and their salts, particularly the barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium or
30 calcium salts. These may be used in any combination.

[0067] Ionomer resin are also particularly preferred in making the golf ball cover.

[0068] Other thermoplastic elastomers that may be used to form the non-butadiene rubber components of the golf ball include thermoplastic polyolefin elastomers.

These are metallocene-catalyzed block copolymers of ethylene and α -olefins having 4 to about 8 carbon atoms prepared by single-site metallocene catalysis of ethylene with a softening comonomer such as hexene-1 or octene-1, for example in a high pressure process in the presence of a catalyst system comprising a cyclopentadienyl-transition metal compound and an alumoxane. Octene-1 is a preferred comonomer to use. These materials are commercially available from ExxonMobil under the tradename ExactTM and from the Dow Chemical Company under the tradename EngageTM.

[0069] Suitable thermoplastic styrene block copolymer elastomers that may be used include poly(styrene-butadiene-styrene), poly(styrene-ethylene-*co*-butylene-styrene), poly(styrene-isoprene-styrene), and poly(styrene-ethylene-*co*-propylene) copolymers. These styrenic block copolymers may be prepared by living anionic polymers with sequential addition of styrene and the diene forming the soft block, for example using butyl lithium as initiator. Thermoplastic styrene block copolymer elastomers are commercially available, for example, under the trademark KratonTM sold by Kraton Polymers U.S. LLC, Houston, TX. Other such elastomers may be made as block copolymers by using polymerizable non-rubber monomers in place of the styrene, including meth(acrylate) esters such as methyl methacrylate and cyclohexyl methacrylate, and other vinyl arylenes, such as alkyl styrenes.

[0070] Particularly useful for the cover are thermoplastic and thermoset polyurethane elastomers such as polyester-polyurethanes, polyether-polyurethanes, and polycarbonate-polyurethanes including, without limitation, polyurethanes polymerized using as polymeric diol reactants polyethers and polyesters including polycaprolactone polyesters. These polymeric diol-based polyurethanes are prepared by reaction of the polymeric diol (polyester diol, polyether diol, polycaprolactone diol, polytetrahydrofuran diol, or polycarbonate diol), one or more polyisocyanates, and, optionally, one or more chain extension compounds. Chain extension compounds, as the term is being used, are compounds having two or more functional groups reactive with isocyanate groups, such as the diols, amino alcohols, and diamines. The polymeric diol-based polyurethane should be substantially linear (i.e., substantially all of the reactants are difunctional).

[0071] Diisocyanates used in making the polyurethane elastomers may be aromatic or aliphatic. Useful diisocyanate compounds used to prepare thermoplastic polyurethanes include, without limitation, isophorone diisocyanate (IPDI), methylene bis-4-cyclohexyl isocyanate (H₁₂MDI), cyclohexyl diisocyanate (CHDI), m-tetramethyl xylene diisocyanate (m-TMXDI), p-tetramethyl xylene diisocyanate (p-TMXDI), 4,4'-methylene diphenyl diisocyanate (MDI, also known as 4,4'-diphenylmethane diisocyanate), 2,4- or 2,6-toluene

diisocyanate (TDI), ethylene diisocyanate, 1,2-diisocyanatopropane, 1,3-diisocyanatopropane, 1,6-diisocyanatohexane (hexamethylene diisocyanate or HDI), 1,4-butylene diisocyanate, lysine diisocyanate, meta-xylylenediisocyanate and para-xylylenediisocyanate (XDI), 4-chloro-1,3-phenylene diisocyanate, 1,5-tetrahydro-naphthalene diisocyanate, 4,4'-dibenzyl diisocyanate, and combinations of these. Nonlimiting examples of higher-functionality polyisocyanates that may be used in limited amounts to produce branched thermoplastic polyurethanes (optionally along with monofunctional alcohols or monofunctional isocyanates) include 1,2,4-benzene triisocyanate, 1,3,6-hexamethylene triisocyanate, 1,6,11-undecane triisocyanate, bicycloheptane triisocyanate, triphenylmethane-4,4',4''-triisocyanate, isocyanurates of diisocyanates, biurets of diisocyanates, allophanates of diisocyanates, and the like.

[0072] Nonlimiting examples of suitable diols that may be used as extenders include ethylene glycol and lower oligomers of ethylene glycol including diethylene glycol, triethylene glycol, and tetraethylene glycol; propylene glycol and lower oligomers of propylene glycol including dipropylene glycol, tripropylene glycol, and tetrapropylene glycol; cyclohexanedimethanol, 1,6-hexanediol, 2-ethyl-1,6-hexanediol, 1,4-butanediol, 2,3-butanediol, 1,5-pentanediol, 1,3-propanediol, butylene glycol, neopentyl glycol, dihydroxyalkylated aromatic compounds such as the bis (2-hydroxyethyl) ethers of hydroquinone and resorcinol; p-xylene- α,α' -diol; the bis (2-hydroxyethyl) ether of p-xylene- α,α' -diol; m-xylene- α,α' -diol, and combinations of these. Other active hydrogen-containing chain extenders that contain at least two active hydrogen groups may be used, for example, dithiols, diamines, or compounds having a mixture of hydroxyl, thiol, and amine groups, such as alkanolamines, aminoalkyl mercaptans, and hydroxyalkyl mercaptans, among others. Suitable diamine extenders include, without limitation, ethylene diamine, diethylene triamine, triethylene tetraamine, and combinations of these. Other typical chain extenders are amino alcohols such as ethanolamine, propanolamine, butanolamine, and combinations of these. The molecular weights of the chain extenders can range from about 60 to about 400. Alcohols and amines are preferred.

[0073] In addition to difunctional extenders, a trifunctional extender such as trimethylolpropane, 1,2,6-hexanetriol and glycerol, or monofunctional active hydrogen compounds such as butanol or dimethylamine, may also be included. When the polyurethane is used to make a thermoplastic component, the amount of trifunctional extender is kept low, and the amount of trifunctional or monofunctional compound employed may be, for example, 5.0

equivalent percent or less based on the total weight of the reaction product and active hydrogen containing groups used.

[0074] The polyester diols used in forming a polyurethane elastomer are in general prepared by the condensation polymerization of one or more polyacid compounds and one or more polyol compounds. The polyacid compounds and polyol compounds should be di-functional, i.e., diacid compounds and diols are used to prepare substantially linear polyester diols, although minor amounts of mono-functional, tri-functional, and higher functionality materials can be included to provide a slightly branched, but uncrosslinked polyester polyol component. Suitable dicarboxylic acids include, without limitation, glutaric acid, succinic acid, malonic acid, oxalic acid, phthalic acid, isophthalic acid, hexahydrophthalic acid, adipic acid, maleic acid, suberic acid, azelaic acid, dodecanedioic acid, their anhydrides and polymerizable esters (e.g., methyl esters) and acid halides (e.g., acid chlorides), and mixtures of these. Suitable polyols include those already mentioned, especially the diols. Typical catalysts for the esterification polymerization are protonic acids, Lewis acids, titanium alkoxides, and dialkyltin oxides.

[0075] A polymeric polyether or polycaprolactone diol reactant for preparing polyurethane elastomers may be obtained by reacting a diol initiator, e.g., 1,3-propanediol or ethylene or propylene glycol, with a lactone or alkylene oxide chain-extension reagent. Lactones that can be ring opened by an active hydrogen are well-known in the art. Examples of suitable lactones include, without limitation, ϵ -caprolactone, γ -caprolactone, β -butyrolactone, β -propiolactone, γ -butyrolactone, α -methyl- γ -butyrolactone, β -methyl- γ -butyrolactone, γ -valerolactone, δ -valerolactone, γ -decanolactone, δ -decanolactone, γ -nonanoic lactone, γ -octanoic lactone, and combinations of these. In one preferred embodiment, the lactone is ϵ -caprolactone. Useful catalysts include those mentioned above for polyester synthesis. Alternatively, the reaction can be initiated by forming a sodium salt of the hydroxyl group on the molecules that will react with the lactone ring. In other embodiments, a diol initiator may be reacted with an oxirane-containing compound or cyclic ether to produce a polyether diol to be used in the polyurethane elastomer polymerization. Alkylene oxide polymer segments include, without limitation, the polymerization products of ethylene oxide, propylene oxide, 1,2-cyclohexene oxide, 1-butene oxide, 2-butene oxide, 1-hexene oxide, tert-butylethylene oxide, phenyl glycidyl ether, 1-decene oxide, isobutylene oxide, cyclopentene oxide, 1-pentene oxide, and combinations of these. The oxirane- or cyclic ether-containing compound can be selected from ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, and combinations of these. The alkylene oxide

polymerization is typically base-catalyzed. The polymerization may be carried out, for example, by charging the hydroxyl-functional initiator compound and a catalytic amount of caustic, such as potassium hydroxide, sodium methoxide, or potassium tert-butoxide, and adding the alkylene oxide at a sufficient rate to keep the monomer available for reaction.

- 5 Two or more different alkylene oxide monomers may be randomly copolymerized by coincidental addition or polymerized in blocks by sequential addition. Homopolymers or copolymers of ethylene oxide or propylene oxide are preferred. Tetrahydrofuran may be polymerized by a cationic ring-opening reaction using such counterions as SbF_6^- , AsF_6^- , PF_6^- , SbCl_6^- , BF_4^- , CF_3SO_3^- , FSO_3^- , and ClO_4^- . Initiation is by formation of a tertiary oxonium ion. The polytetrahydrofuran segment can be prepared as a “living polymer” and
- 10 terminated by reaction with the hydroxyl group of a diol such as any of those mentioned above. Polytetrahydrofuran is also known as polytetramethylene ether glycol (PTMEG).

[0076] Aliphatic polycarbonate diols that may be used in making a polyurethane elastomer may be prepared by the reaction of diols with dialkyl carbonates (such as diethyl

15 carbonate), diphenyl carbonate, or dioxolanones (such as cyclic carbonates having five- and six-member rings) in the presence of catalysts like alkali metal, tin catalysts, or titanium compounds. Useful diols include, without limitation, any of those already mentioned. Aromatic polycarbonates are usually prepared from reaction of bisphenols, e.g., bisphenol A, with phosgene or diphenyl carbonate.

20 [0077] In various embodiments, the polymeric diol can have a weight average molecular weight of at least about 500, or at least about 1000, or at least about 1800 and a weight average molecular weight of up to about 10,000, but polymeric diols having weight average molecular weights of up to about 5000, or up to about 4000, may also be used. The polymeric diol can have a weight average molecular weight in the range from about 500 to

25 about 10,000, or from about 1000 to about 5000, or from about 1500 to about 4000. The weight average molecular weights may be determined by ASTM D-4274.

[0078] The reaction of the polyisocyanate, polymeric diol, and diol or other chain extension agent is typically carried out in the presence of a catalyst. Typical catalysts for this reaction include organotin catalysts such as stannous octoate, dibutyl tin dilaurate, dibutyl tin

30 diacetate, dibutyl tin oxide, tertiary amines, zinc salts, and manganese salts. Generally, for elastomeric polyurethanes, the ratio of polymeric diol, such as polyester diol, to extender can be varied within a relatively wide range depending largely on the desired hardness of the final polyurethane elastomer. For example, the equivalent proportion of polyester diol to extender may be within the range of 1:0 to 1:12 or from 1:1 to 1:8. The diisocyanate(s) employed are

proportioned such that the overall ratio of equivalents of isocyanate to equivalents of active hydrogen containing materials is within the range of 1:1 to 1:1.05 or within the range of 1:1 to 1:1.02. The polymeric diol segments typically are from about 35% to about 65% by weight of the polyurethane polymer or from about 35% to about 50% by weight of the polyurethane polymer.

[0079] The cover or other golf ball component may alternatively be made using a polyurea elastomer. Suitable polyurea elastomers may be prepared by reaction of one or more polymeric diamines or polyols with one or more of the polyisocyanates already mentioned and one or more diamine extenders. Nonlimiting examples of suitable diamine extenders include ethylene diamine, 1,3-propylene diamine, 2-methyl-pentamethylene diamine, hexamethylene diamine, 2,2,4- and 2,4,4-trimethyl-1,6-hexane diamine, imino-bis(propylamine), imido-bis(propylamine), N-(3-aminopropyl)-N-methyl-1,3-propanediamine), 1,4-bis(3-aminopropoxy)butane, diethyleneglycol-di(aminopropyl)ether, 1-methyl-2,6-diamino-cyclohexane, 1,4-diamino-cyclohexane, 1,3- or 1,4-bis(methylamino)-cyclohexane, isophorone diamine, 1,2- or 1,4-bis(sec-butylamino)-cyclohexane, N,N'-diisopropyl-isophorone diamine, 4,4'-diamino-dicyclohexylmethane, 3,3'-dimethyl-4,4'-diamino-dicyclohexylmethane, N,N'-dialkylamino-dicyclohexylmethane, and 3,3'-diethyl-5,5'-dimethyl-4,4'-diamino-dicyclohexylmethane. Polymeric diamines include polyoxyethylene diamines, polyoxypropylene diamines, poly(oxyethylene-oxypropylene) diamines, and poly(tetramethylene ether) diamines. The amine- and hydroxyl-functional extenders already mentioned may be used as well. Generally, as before, trifunctional reactants are limited and may be used in conjunction with monofunctional reactants to prevent crosslinking.

[0080] Suitable thermoplastic polyamide elastomers may be obtained by: (1) polycondensation of (a) a dicarboxylic acid, such as oxalic acid, adipic acid, sebacic acid, terephthalic acid, isophthalic acid, 1,4-cyclohexanedicarboxylic acid, or any of the other dicarboxylic acids already mentioned with (b) a diamine, such as ethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, or decamethylenediamine, 1,4-cyclohexanediamine, m-xylylenediamine, or any of the other diamines already mentioned; (2) a ring-opening polymerization of a cyclic lactam, such as ϵ -caprolactam or ω -lauro lactam; (3) polycondensation of an aminocarboxylic acid, such as 6-aminocaproic acid, 9-aminononanoic acid, 11-aminoundecanoic acid, or 12-aminododecanoic acid; or (4) copolymerization of a cyclic lactam with a dicarboxylic acid and a diamine to prepare a carboxylic acid-functional polyamide block, followed by reaction with a polymeric

ether diol (polyoxyalkylene glycol) such as any of those already mentioned. Polymerization may be carried out, for example, at temperatures of from about 180° C. to about 300° C.

Specific examples of suitable polyamide blocks include NYLON 6, NYLON 66, NYLON 610, NYLON 11, NYLON 12, copolymerized NYLON, NYLON MXD6, and NYLON 46

block copolymer elastomers. Thermoplastic poly(ether amide) block copolymer elastomers (PEBA) are commercially available under the trademark Pebax® from Arkema.

[0081] Thermoplastic polyester elastomers have blocks of monomer units with low chain length that form the crystalline regions and blocks of softening segments with monomer units having relatively higher chain lengths. Thermoplastic polyester elastomers are commercially available under the trademark Hytrel® from DuPont.

[0082] A combination of thermoplastic elastomers may be used. In one embodiment, the first or second thermoplastic material includes a combination of a metal ionomer of a copolymer of ethylene and at least one of acrylic acid and methacrylic acid, a metallocene-catalyzed copolymer of ethylene and an α -olefin having 4 to about 8 carbon atoms, and a metal salt of an unsaturated fatty acid. This material may be prepared as described in Statz et al., U.S. 7,375,151 or as described in Kennedy, "Process for Making Thermoplastic Golf Ball Material and Golf Ball with Thermoplastic Material, U.S. Patent Appl. No. 13,825,112, filed 15 March 2013, the entire contents of both being incorporated herein by reference.

[0083] The elastomer compositions may further comprise small amounts of optional materials commonly used and well known in the polymer art, however. Such materials include conventional additives used in making polymeric compositions for golf balls including plasticizers, stabilizers including viscosity stabilizers and hydrolytic stabilizers, primary and secondary antioxidants such as those mentioned above, pigments or other coloring agents, processing aids, slip additives, antiblock agents such as silica or talc (which may also serve as fillers), release agents, inorganic fillers as described above, and other components that provide useful qualities. These conventional ingredients may be present in the compositions in quantities that are generally from 0.01 to 15 weight %, or from 0.01 to 5 weight % or 0.01 to 10 weight %, based on the total weight of the composition. The incorporation of these optional materials into the thermoplastic elastomer compositions may be carried out by any known process, for example, by dry blending, by extruding a mixture of the various constituents, by the conventional masterbatch technique, or the like.

[0084] The selected thermoplastic elastomer composition is molded into a golf ball component. In a preferred embodiment, a core is formed of the highly neutralized

polymer composition and an intermediate layer is formed by molding and curing the polybutadiene rubber composition in a layer around the core. In an alternative embodiment, a core is prepared by compression molding and curing (i.e., crosslinking, also called vulcanizing) the polybutadiene rubber composition, then an intermediate layer of a thermoplastic polymer composition, for example an ionomer composition such as the highly neutralized polymer composition, is molded around the crosslinked rubber core.

[0085] The cover may be injection molded around the core and any intermediate layers. The molding temperature is generally in a range of from 150 to 250 °C. When injection molding a thermoset polyurethane or polyurea cover is carried out, it is desirable though not essential to carry out molding in a low-humidity environment such as by purging with an inert gas (e.g., nitrogen) or a low-temperature gas (e.g., low dew-point dry air), or by vacuum treating, some or all places on the resin paths from the resin feed area to the mold interior. Illustrative, non-limiting, examples of the medium used for transporting the resin include low-moisture gases such as low dew-point dry air or nitrogen. By carrying out molding in such a low-humidity environment, reaction by the isocyanate groups is kept from proceeding before the resin has been charged into the mold interior. As a result, polyisocyanate in which the isocyanate groups are present in an unreacted state is included to some degree in the resin molded piece, thus making it possible to reduce variable factors such as an unwanted rise in viscosity and enabling the real crosslinking efficiency to be enhanced.

[0086] Alternatively the cover can be applied by initially forming two hemispherical shells, then covering the core with these shells and molding under applied pressure and heat.

[0087] The dimples arranged on the cover surface, while not subject to any particular limitation, can number from 250 to 350, or from 300 to 350, or from 318 to 328. Any one or combination of two or more dimple shapes, including circular shapes, various polygonal shapes, dewdrop shapes and oval shapes, may be suitably used. For example, when circular dimples are used, a dimple diameter of at least about 2.5 mm but not more than about 6.0 mm may be suitably selected. By using from three to five or more types of dimples, the dimples can be made to cover the spherical surface in a well-balanced and uniform manner. The types of dimples are not subject to any particular limitation, although the dimples may be disposed on the spherical surface in a polyhedral arrangement suitable for dimple placement, such as a repeating pattern of unit polygons (e.g., unit triangles, unit pentagons). It is also possible to use dimples which all have slightly different diameters. In such a case, the number of dimple types may be set to twenty or more. In order to fully

manifest the aerodynamic properties, it is desirable for the ratio of the sum of the individual dimple surface areas, each defined as the surface area of the flat plane circumscribed by the edge of the dimple, relative to the spherical surface area of the ball were it to have no dimples thereon to be at least 70%, or 75%.

5 **[0088]** The foregoing description of the embodiments has been provided for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention. Individual elements or features of a particular embodiment are generally not limited to that particular embodiment, but, where applicable, are interchangeable and can be used in a selected embodiment, even if not specifically shown or described. The same may
10 also be varied in many ways. Such variations are not to be regarded as a departure from the invention, and all such modifications are intended to be included within the scope of the invention.

CLAIMS

What is claimed is:

1. A golf ball comprising a core, a cover, and optionally one or more intermediate layers between the core and the cover, wherein the core, one or a plurality of intermediate layers, or a combination thereof is formed by crosslinking a rubber composition comprising
 - (a) 100 parts by weight of a polybutadiene having a cis-1,4 bond content of about 85% to 100%;
 - (b) from about 10 to about 50 parts by weight of (i) a zinc, magnesium, or calcium salt of a first carboxylic acid having at least two ethylenically unsaturated bonds and, optionally, (ii) a zinc, magnesium, or calcium salt of a second carboxylic acid having one ethylenically unsaturated bond that is α,β to a carbonyl of a carboxyl group, wherein (b)(i) is from about 50% by weight to 100% by weight of the combined weights of (b)(i) and (b)(ii);
 - (c) a free radical initiator; and
 - (d) an inorganic zinc, magnesium, or calcium compound.
2. A golf ball according to claim 1, wherein the first carboxylic acid comprises at least two conjugated, ethylenically unsaturated bonds.
3. A golf ball according to claim 1 or claim 2, wherein one of the ethylenically unsaturated bonds of the first carboxylic acid is conjugated with a carbonyl group.
4. A golf ball according to any of claims 1 to 3, wherein the first carboxylic acid is a monocarboxylic acid, or (b)(ii) is present and the second carboxylic acid is a monocarboxylic acid, or both.
5. A golf ball according to any of claims 1 to 4, wherein (b)(i) comprises a zinc salt of a linear carboxylic acid having at least 6 carbon atoms.
6. A golf ball according to any of claims 1 to 5, wherein (b)(ii) is present and comprises a member selected from the group consisting of zinc diacrylate, zinc dimethacrylate, and combinations thereof.

7. A golf ball according to any of claims 1 to 6, wherein (b)(ii) is present and comprises zinc diacrylate and wherein the rubber composition further includes zinc stearate.

8. A golf ball according to any of claims 1 to 7, wherein (b)(ii) is present and (b)(i) is from about 50% by weight to about 90% by weight of the combined weights of (b)(i) and (b)(ii).

9. A golf ball according to any of claims 1 to 8, wherein the inorganic compound (d) comprises zinc oxide.

10. A golf ball according to any of claims 1 to 9, wherein the rubber composition comprises from about 2 to about 30 parts by weight of the inorganic compound (d).

11. A method of making a golf ball having a core, a cover, and, optionally, at least one intermediate layer between the core and the cover, comprising:

forming a rubber composition comprising

- (a) 100 parts by weight of a polybutadiene having a cis-1,4 bond content of about 85% to 100%;
- (b) from about 10 to about 50 parts by weight of (i) a zinc, magnesium, or calcium salt of a first carboxylic acid having at least two ethylenically unsaturated bonds and, optionally, (ii) a zinc, magnesium, or calcium salt of a second carboxylic acid having one ethylenically unsaturated bond that is α,β to a carbonyl of a carboxyl group, wherein (b)(i) is from about 50% by weight to 100% by weight of the combined weights of (b)(i) and (b)(ii);
- (c) a free radical initiator; and
- (d) an inorganic zinc, magnesium, or calcium compound;

molding and curing the rubber composition into a core, one or a plurality of intermediate layers, or a combination thereof; and

applying the cover.

12. A method of making a golf ball according to claim 11, wherein the first carboxylic acid comprises at least two conjugated, ethylenically unsaturated bonds.

13. A method of making a golf ball according to claim 11 or claim 12, wherein one of the ethylenically unsaturated bonds of the first carboxylic acid is conjugated with a carbonyl group.

5 14. A method of making a golf ball according to any of claims 11 to 13, wherein the first carboxylic acid is a monocarboxylic acid, or (b)(ii) is present and the second carboxylic acid is a monocarboxylic acid, or both.

10 15. A method of making a golf ball according to any of claims 11 to 14, wherein (b)(i) comprises a zinc salt of a linear carboxylic acid having at least 6 carbon atoms.

16. A method of making a golf ball according to any of claims 11 to 15, wherein (b)(ii) is present and comprises a member selected from the group consisting of zinc diacrylate, zinc dimethacrylate, and combinations thereof.

15 17. A method of making a golf ball according to any of claims 11 to 16, wherein (b)(ii) is present and comprises zinc diacrylate and wherein the rubber composition further includes zinc stearate.

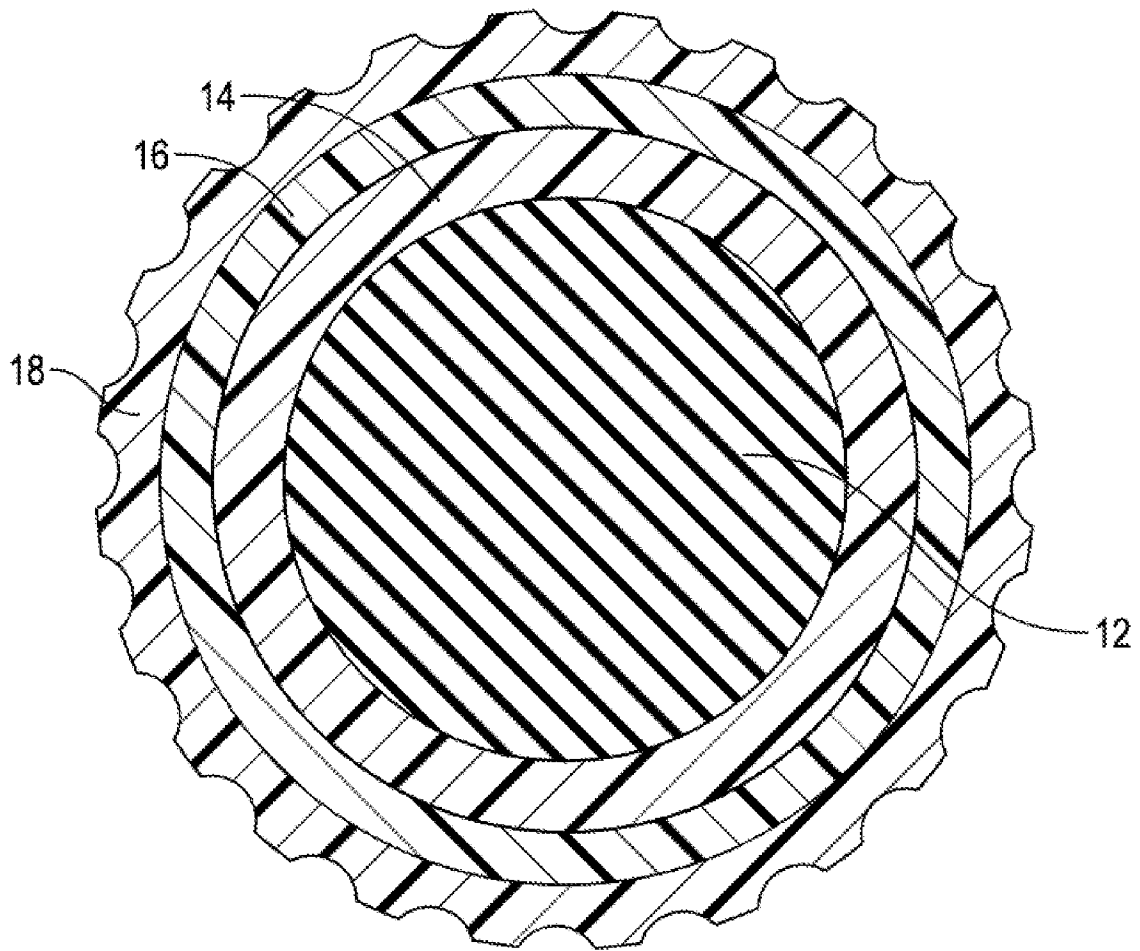
20 18. A method of making a golf ball according to any of claims 11 to 17, wherein (b)(ii) is present and (b)(i) is from about 50% by weight to about 90% by weight of the combined weights of (b)(i) and (b)(ii).

25 19. A method of making a golf ball according to any of claims 11 to 17, wherein the inorganic compound (d) comprises zinc oxide.

30 20. A method of making a golf ball according to any of claims 11 to 19, wherein the rubber composition comprises from about 2 to about 30 parts by weight of the inorganic compound (d).

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FIG.



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/023896

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K5/098 C08L9/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 844 471 A (MELVIN TERENCE [US] ET AL) 4 July 1989 (1989-07-04) claims 13-24; examples 1-9 -----	1-20
X	US 4 852 884 A (SULLIVAN MICHAEL J [US]) 1 August 1989 (1989-08-01) claims 13-24; examples 1-9 -----	1-20
X	WO 98/35727 A1 (HANSBERGER PRECISION GOLF INC [US]) 20 August 1998 (1998-08-20) page 4, last two lines; claims 1,2; example 2 -----	1-20
X	US 6 612 940 B1 (NESBITT R DENNIS [US] ET AL) 2 September 2003 (2003-09-02) column 11, line 43; claims 1,2; tables 11, 13, 15, 17, 19, 21, 24 -----	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

12 June 2015

Date of mailing of the international search report

24/06/2015

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2015/023896

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4844471	A	04-07-1989	NONE	
US 4852884	A	01-08-1989	NONE	
WO 9835727	A1	20-08-1998	NONE	
US 6612940	B1	02-09-2003	NONE	