Abstract: Scuff-resistant golf ball covers and methods of manufacturing golf balls are described. The cover is made of a thermoplastic polymeric portion including at least one first, high molecular weight copolymer of ethylene/5-12 percent by weight acrylic or methacrylic acid or both/5-40 percent by weight alkyl acrylate or methacrylate or both; optionally at least one second, low molecular weight copolymer of ethylene/3-25 percent by weight acrylic or methacrylic acid or both; and a high molecular weight dipolymer of ethylene/acrylic acid that has a molar fraction of the acrylic acid monomer units within about 10% of a molar fraction of the α,β-ethylenically unsaturated carboxylic acid monomer units of the at least one first copolymer. The acid groups of all acid monomer units are neutralized 30% to about 75% on a molar basis by magnesium cations, calcium cations, zinc cations, or a combination of these cations.
GOLF BALL WITH SCUFF-RESISTANT COVER

[0001] The present application claims the benefit of U.S. Provisional Application No. 61/980,849, filed April 17, 2014.

FIELD

[0002] The disclosed technology relates to golf balls with scuff-resistant covers made from ionomer resins and methods of making golf balls with scuff-resistant covers.

BACKGROUND

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

[0004] Golf ball covers formed from polyurethane compositions combine good scuff resistance with a softness that enables spin control and good playability in “premium” balls for the more skilled player. Polyurethane covers are low in resilience, however, and thermoset polyurethane covers are more difficult to process than thermoplastic ionomer resins. The material costs are higher, as well, and therefore golf balls with polyurethane covers are also more expensive to manufacture.

[0005] Ionomeric resins (ionomers) are useful materials for the construction of golf balls and other articles. Ionomers are ionic copolymers that are obtained by copolymerization of an olefin such as ethylene with an unsaturated carboxylic acid such as acrylic acid (AA), methacrylic acid (MAA), or maleic acid. Optionally, one or more softening monomers, such as alkyl acrylates, may be included in the olefin-acid copolymer. At least a portion of the carboxylic acid groups in the copolymer are neutralized with a neutralizing agent to form carboxylate groups having counter cations, such as for example zinc cations or sodium cations. The resulting ionomer is a thermoplastic resin exhibiting favorable properties for use in golf balls. For example, golf balls constructed using ionomeric materials have improved resilience and cut resistance durability as compared with golf balls constructed with balata. As a result of their resilience, toughness, durability and good flight characteristics, ionomers have become materials of choice for the construction of golf balls over the traditional balata, trans-polyisoprene, natural, and synthetic rubbers.

[0006] Harder ionomeric resins have been blended with softer ionomeric resins to make a more durable golf ball cover material. U.S. Patents Nos. 4,884,814 and 5,120,791, for example, are directed to cover compositions containing blends of hard and soft ionomer...
resins. The hard copolymers typically are ionomers of dipolymers made from an olefin and an unsaturated carboxylic acid and the soft copolymers typically are ionomers of first copolymers made from an olefin, an unsaturated carboxylic acid, and an unsaturated carboxylic acid ester. While golf balls formed from hard-soft ionomer blends have good cut resistance, they tend to become scuffed more readily than covers made of hard ionomer alone. U.S. Patent No. 5,902,855 is directed to golf balls with scuff resistant covers comprising blends of ionomers with Shore D hardness of about 40 to 64 units. Ichikawa et al., US Patent No. 6,130,294 teaches blending a soft, magnesium-neutralized ethylene/acrylic acid, methacrylic acid, or both acrylic acid and methacrylic acid/acrylate first copolymer ionomer with a hard, magnesium-neutralized ethylene/acrylic acid, methacrylic acid, or both acrylic acid and methacrylic acid copolymer to make a blend having a Shore D hardness of 44-60. A golf ball with this cover is said to minimize restitution loss and has increased initial velocity, spin receptivity, good feel, and scuff resistance.

Bimodal ionomer compositions may also be used as scratch and scuff-resistant surface layers of a variety of articles. Chen, US Pat. Appl. Publ. 2004/0132552 discloses a cover with a "bimodal" ionomer composition including the high molecular weight first copolymer and the low molecular dipolymer achieves enhanced processability, resilience, stability, and scuff resistance. Chen, U.S. Patent Application Publication No. 2009/0130355 discloses compositions that comprise an ethylene α,β-ethylenically unsaturated C₃₋₈ carboxylic acid copolymer having weight average molecular weight (Mw) of about 80,000 to about 500,000 Da (high molecular weight copolymer) and an ethylene α,β-ethylenically unsaturated C₃₋₈ carboxylic acid copolymer having (Mw) of about 2,000 to about 30,000 Da (low molecular weight copolymer). In some cases, however, these bimodal compositions are too soft to make good golf ball covers. Bimodal ionomer compositions and their use in golf balls are also described in Chen, U.S. Patents Nos. 6,562,906; 6,762,246; 7,037,967; 7,273,903; 7,488,778; 8,193,283; 8,410,219; and 8,410,220.

Recently, Chen, US Pat. Appl. Publ. 2011/0306442 proposed a ternary mixture of a high molecular weight first copolymer of ethylene, a C₃₋₈ α,β-ethylenically unsaturated carboxylic acid, and a softening comonomer; a high molecular weight dipolymer of ethylene and acrylic or methacrylic acid; and a low molecular weight dipolymer of ethylene and acrylic or methacrylic acid, the mixture being neutralized at least 70% with predominantly zinc cations. Chen, US Patent 8,410,219 teaches that the melt flow rate of such a ternary composition can be increased by including non-zinc cations, but such a modification is not said to be effective for improving scuff resistance.
Kasashima et al., US Pat. 8,414,425 notes the difficulty of producing a soft golf ball having an excellent feel that achieves both a good flight performance and has an excellent durability to repeated impact. A softer cover produces a better feel, but lacks durability and diminishes rebound, while a harder cover does not have the desired feel and is prone to early cracking. The Kasahima inventors focused on a layer underlying the cover for improving rebound, while filling an ionomer-based cover with inorganic granular filler to achieve a desired Shore D hardness. Saski et al., US Patent 6,905,425, approach the problem by including a significant amount of a thermoplastic styrene block elastomer such as SBS.

Despite continuing efforts to bring the scuff resistance of the less expensive, more easily processed ionomer covers up to par with polyurethane covers, substantial improvements in scuff resistance of ionomer covers have been elusive to date.

SUMMARY

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

Disclosed are golf balls and methods of manufacturing the disclosed golf balls. The disclosed golf balls have a core and a cover having a composition with a thermoplastic polymeric portion consisting of or consisting essentially of a component (a) of (i) at least one first copolymer and, optionally, (ii) at least one second copolymer and a component (b) of a dipolymer. The at least one first copolymer (a)(i) is formed of ethylene monomer units, from about 5 to about 12 percent by weight of α,β-ethylenically unsaturated carboxylic acid monomer units selected from acrylic acid monomer units, methacrylic acid monomer units, or a combination of acrylic acid monomer units and methacrylic acid monomer units, and from about 5 to about 40 percent by weight of monomer units of at least one alkyl acrylate or of at least one alkyl methacrylate or of a combination of at least one alkyl acrylate and at least one alkyl methacrylate. The at least one first copolymer (a)(i) has a weight average molecular weight of from about 80,000 to about 500,000 daltons. The at least one second copolymer (a)(ii) is formed of ethylene monomer units and from about 3 to about 25 percent by weight of α,β-ethylenically unsaturated carboxylic acid monomer units selected from acrylic acid monomer units, methacrylic acid monomer units, or a combination of acrylic acid monomer units and methacrylic acid monomer units. The at least one second copolymer (a)(ii) has a weight average molecular weight of from about 2000 to about 30,000 daltons. The at least one dipolymer (b) is formed of ethylene monomer units and acrylic acid monomer units. The at least one dipolymer (b) has a weight average molecular weight of from about 80,000 to about 500,000 daltons and has a molar fraction of acrylic acid monomer
units within ± about 10% of a molar fraction of α,β-ethylenically unsaturated carboxylic acid monomer units of the at least one first copolymer (a)(i). The molar fraction of α,β-ethylenically unsaturated carboxylic acid monomer units of the first copolymer (a)(i) is the moles of α,β-ethylenically unsaturated carboxylic acid monomer units of all first copolymers (a)(i) divided by the total moles of all constituent monomer units of all first copolymers (a)(i). Similarly, the molar fraction of acrylic acid monomer units of the dipolymer (b) is the moles of acrylic acid monomer units of all dipolymers (b) divided by the total moles of all constituent monomer units of all dipolymers (b). The at least one first copolymer (a)(i) is from about 80 to 100 percent by weight of the sum of the weights of (a)(i) and (a)(ii). From about 30% to about 75% on a molar basis of all acid groups of (a) and (b) are neutralized with cations selected from magnesium cations, calcium cations, zinc cations, and combinations of these cations. The α,β-ethylenically unsaturated carboxylic acid monomer of (a)(i) and the α,β-ethylenically unsaturated carboxylic acid monomer of (a)(ii) may be selected independently of each other. For example, one could have only acrylic acid monomer units while the other has only methacrylic acid monomer units, or both could have all acrylic acid monomer units or all methacrylic acid monomer units, or both could have a combination of acrylic acid and methacrylic acid monomer units in which the relative amounts of the acrylic acid monomer units and the methacrylic acid monomer units could be the same for both of or different in each of the first copolymer (a)(i) and the second copolymer (a)(ii).

The disclosed method of manufacturing a golf ball comprises forming around a core a cover from a thermoplastic polymeric portion consisting of or consisting essentially of a component (a) of (i) at least one first copolymer and, optionally, (ii) at least one second copolymer and a component (b) of a dipolymer. The at least one first copolymer (a)(i) is formed of ethylene monomer units, from about 5 to about 12 percent by weight of α,β-ethylenically unsaturated carboxylic acid monomer units selected from acrylic acid monomer units, methacrylic acid monomer units, or a combination of acrylic acid monomer units and methacrylic acid monomer units, and from about 5 to about 40 percent by weight of monomer units of at least one alkyl acrylate or of at least one alkyl methacrylate or of a combination of at least one alkyl acrylate and at least one alkyl methacrylate. The at least one first copolymer (a)(i) has a weight average molecular weight of from about 80,000 to about 500,000 daltons. The at least one second copolymer (a)(ii) is formed of ethylene monomer units and from about 3 to about 25 percent by weight of α,β-ethylenically unsaturated carboxylic acid monomer units selected from acrylic acid monomer units, methacrylic acid monomer units, or a combination of acrylic acid monomer units and methacrylic acid monomer units, or a combination of acrylic acid monomer units and
methacrylic acid monomer units. The at least one second copolymer (a)(ii) has a weight average molecular weight of from about 2000 to about 30,000 daltons. The at least one dipolymer (b) is formed of ethylene monomer units and acrylic acid monomer units. The at least one dipolymer (b) has a weight average molecular weight of from about 80,000 to about 500,000 daltons and has a molar fraction of acrylic acid monomer units within ± about 10% of a molar fraction of α,β-ethylenically unsaturated carboxylic acid monomer units of the at least one first copolymer (a)(i). The molar fraction of α,β-ethylenically unsaturated carboxylic acid monomer units of the first copolymer (a)(i) is the moles of α,β-ethylenically unsaturated carboxylic acid monomer units of all first copolymers (a)(i) divided by the total moles of all constituent monomer units of all first copolymers (a)(i). Similarly, the molar fraction of acrylic acid monomer units of the dipolymer (b) is the moles of acrylic acid monomer units of all dipolymers (b) divided by the total moles of all constituent monomer units of all dipolymers (b). The at least one first copolymer (a)(i) is from about 80 to 100 percent by weight of the sum of the weights of (a)(i) and (a)(ii). From about 30% to about 75% on a molar basis of all acid groups of (a) and (b) are neutralized with cations selected from magnesium cations, calcium cations, zinc cations, and combinations of these cations. The α,β-ethylenically unsaturated carboxylic acid monomer of (a)(i) and the α,β-ethylenically unsaturated carboxylic acid monomer of (a)(ii) may be selected independently of each other. For example, one could have only acrylic acid monomer units while the other has only methacrylic acid monomer units, or both could have all acrylic acid monomer units or all methacrylic acid monomer units, or both could have a combination of acrylic acid and methacrylic acid monomer units in which the relative amounts of the acrylic acid monomer units and the methacrylic acid monomer units could be the same for both of or different in each of the first copolymer (a)(i) and the second copolymer (a)(ii).

[0014] The golf ball cover's component (a) can be or can consist essentially of the at least one first copolymer (a)(i). Alternatively, the golf ball cover's component (a) can include the at least one second copolymer (a)(ii), which may be present in from a finite amount more than zero to about 20 percent by weight of the sum of the weights of the at least one first copolymer (a)(i) and the at least one second copolymer (a)(ii). Copolymer (a)(i) can be 100 percent by weight and copolymer (a)(ii) 0 percent by weight of the sum of the weights of (a)(i) and (a)(ii). In other embodiments, the at least one second copolymer (a)(ii) can be from about 5 to about 20 percent by weight, based on the sum of the weights of (a)(i) and (a)(ii) or the at least one second copolymer (a)(ii) can be from about 5 to about 15 percent by weight, based on the sum of the weights of (a)(i) and (a)(ii). The at least one dipolymer (b) can be from about 10 to about 90 percent by weight, based on the combined
weights of components (a) (the at least one first copolymer (a)(i) and, if present, the at least one second copolymer (a)(ii)) and (b) (the at least one dipolymer (b)). The at least one dipolymer (b) can be from about 30 to about 65 percent by weight, based on the combined weights of components (a) (the at least one first copolymer (a)(i) and, if present, the at least one second copolymer (a)(ii)) and (b) (the at least one dipolymer (b)).

[0015] The at least one first copolymer (a)(i) monomer units of at least one alkyl acrylate or of at least one alkyl methacrylate or of a combination of at least one alkyl acrylate and at least one alkyl methacrylate can be or include n-butyl acrylate monomer units or isobutyl acrylate monomer units, or both. The at least one first copolymer (a)(i) can be or include a copolymer selected from the group consisting of copolymers of ethylene/acrylic acid/n-butyl acrylate, copolymers of ethylene/methacrylic acid/n-butyl acrylate, copolymers of ethylene/methacrylic acid/isobutyl acrylate, copolymers of ethylene/acrylic acid/isobutyl acrylate, all of which may be used in any combination.

[0016] In various embodiments, the α,β-ethylenically unsaturated carboxylic acid monomer units of one or both of the at least one first copolymer (a)(i) and the at least one second copolymer (a)(ii) are acrylic acid monomer units.

[0017] In various embodiments, the neutralizing cations are selected from magnesium cations, calcium cations, and combinations thereof. In certain embodiments, the neutralizing cations are all calcium cations. The neutralizing metal cations can all be calcium cations. The neutralizing metal cations can all be magnesium cations. The neutralizing metal cations can all be calcium cations. The neutralizing metal cations can all be zinc cations. For example, about 50% to 100% on a molar basis of the neutralizing cations can be magnesium cations, calcium cations, or a combination of magnesium and calcium cations. From about 50% to about 100% on a molar basis of the neutralizing cations can be magnesium cations. From about 50% to about 100% on a molar basis of the neutralizing metal cations can be calcium cations. From about 50% to about 100% on a molar basis of the neutralizing metal cations can be zinc cations.

[0018] The at least one first copolymer (a)(i) can have from about 8 to about 12 percent by weight of α,β-ethylenically unsaturated carboxylic acid monomer units.

[0019] The at least one dipolymer (b) can have a molar fraction of acrylic acid monomer units within ± about 5% of a molar fraction of α,β-ethylenically unsaturated carboxylic acid monomer units of the at least one first copolymer (a)(i). The at least one dipolymer (b) can have a molar fraction of acrylic acid monomer units within ± about 3% of a molar fraction of α,β-ethylenically unsaturated carboxylic acid monomer units of the at least one first copolymer (a)(i).
The at least one first copolymer (a)(i) can have from about 8 to about 12 percent by weight of \( \alpha,\beta \)-ethylenically unsaturated carboxylic acid monomer units, and the at least one dipolymer (b) can have a molar fraction of acrylic acid monomer units within \( \pm \) about 3% of a molar fraction of \( \alpha,\beta \)-ethylenically unsaturated carboxylic acid monomer units of the at least one first copolymer (a)(i). The at least one second copolymer (a)(ii) can have from about 5 to about 20 weight percent of \( \alpha,\beta \)-ethylenically unsaturated carboxylic acid monomer units. The at least one second copolymer (a)(ii) can have from about 8 to about 18 weight percent of \( \alpha,\beta \)-ethylenically unsaturated carboxylic acid monomer units. The at least one first copolymer (a)(i) can have from about 8 to about 12 weight percent of \( \alpha,\beta \)-ethylenically unsaturated carboxylic acid monomer units, and the at least one second copolymer (a)(ii) can have from about 8 to about 18 weight percent of \( \alpha,\beta \)-ethylenically unsaturated carboxylic acid monomer units. The at least one second copolymer (a)(ii) can have from about 8 to about 18 weight percent of \( \alpha,\beta \)-ethylenically unsaturated carboxylic acid monomer units, and the at least one dipolymer (b) can have a molar fraction of acrylic acid monomer units within \( \pm \) about 3% of a molar fraction of \( \alpha,\beta \)-ethylenically unsaturated carboxylic acid monomer units of the at least one first copolymer (a)(i).

The weight average molecular weight of the at least one first copolymer (a)(i) can be from about 200,000 to about 400,000 daltons. The at least one first copolymer can have a weight average molecular weight of from about 150,000 daltons to about 350,000 daltons. The at least one first copolymer can have a polydispersity \( \text{Mw/Mn} \) of from about 1 to about 15. The at least one first copolymer can have a weight average molecular weight of from about 150,000 daltons to about 350,000 daltons, a polydispersity \( \text{Mw/Mn} \) of from about 1 to about 3, and can have from about 8 to about 9 wt% of the \( \alpha,\beta \)-ethylenically unsaturated carboxylic acid monomer units present.

The weight average molecular weight of the at least one second copolymer (a)(ii) can be from about 5000 daltons to about 25,000 daltons. The number average molecular weight of the at least one second copolymer can be from about 10,000 daltons to about 20,000 daltons. The polydispersity \( \text{Mw/Mn} \) of the second copolymer can be from about 1 to about 15. The polydispersity of the second copolymer can be from about 1 to about 3. The number average molecular weight of the at least one second copolymer can be from about 10,000 daltons to about 20,000 daltons, and the polydispersity of the second copolymer can be from about 1 to about 3.
can be from about 200,000 to about 400,000 daltons. The weight average molecular weight of the at least one dipolymer (b) can be from about 150,000 daltons to about 350,000 daltons. The weight average molecular weight of the at least one dipolymer (b) can have a polydispersity of from about 1 to about 15. The at least one dipolymer (b) can have a polydispersity of about 1 to about 3. The weight average molecular weight of the at least one dipolymer (b) can be from about 150,000 daltons to about 350,000 daltons, and a polydispersity of about 1 to about 3.

[0024] The weight average molecular weight of the at least one first copolymer (a)(i) can be from about 200,000 to about 400,000 daltons, and the weight average molecular weight of the at least one dipolymer (b) can be from about 200,000 to about 400,000 daltons.

[0025] The cover of the golf ball can have a thickness of from about 1 mm to about 3 mm.

[0026] An "ethyleiiieally unsaturated bond" is a carbon-to-carbon double bond. "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" includes any and all combinations of one or more of the 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."

A description of a copolymer with reference to its constituent comonomers
or to the amounts of its constituent comonomers means that the copolymer contains
copolymersized units of the specified comonomers which may be contained in a specified
amount. The term "dipolymer" refers to polymers consisting essentially of two different
copolymerized monomers and the term "copolymer" refers to polymers having different
copolymerized monomers.

The term "Mw" means weight average molecular weight and the term
"Mn" means number average molecular weight. In this description, "low molecular weight"
is used to refer to polymers that have a weight average molecular weight (Mw) of from about
2000 to about 30,000 daltons and "high molecular weight" is used to refer to polymers that
have a molecular weight (Mw) of from about 80,000 to about 500,000 daltons. Number
average molecular weight and weight average molecular weight are determined by gel
permeation chromatography (GPC) using polystyrene standards.

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

The drawings illustrate some aspects of the disclosed technology.
The FIG. is a schematic, cross-sectional view of a golf ball.
The parts of the figure are not necessarily to scale.

DETAILED DESCRIPTION

A detailed description including exemplary, nonlimiting embodiments
follows. Unless stated otherwise, amount are by weight.
The disclosed golf ball has an ionomer-resin cover with improved scuff
resistance. The golf ball has a core, the cover, and optionally one or more intermediate layers
between the core and the cover. For example, the golf ball may be a four-piece golf ball such
as the one illustrated in the Figure, in which 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. The cover 18 is formed from a composition having the disclosed thermoplastic polymeric portion consisting essentially of a high molecular weight first copolymer (a)(i) formed of ethylene monomer units, about 5 to about 12 percent by weight α,β-ethylenically unsaturated carboxylic acid monomer units selected from acrylic acid monomer units, methacrylic acid monomer units, and combinations of acrylic acid and methacrylic acid monomer units, and about 3 to about 40 weight percent of at least one member selected from the group consisting of alkyl acrylate monomer units, alkyl methacrylate monomer units, and combinations of alkyl acrylate monomer units, alkyl methacrylate monomer units; a high molecular weight dipolymer (b) formed of ethylene monomer units and acrylic acid monomer units having a molar fraction of acrylic acid monomer units within ± about 10% of a molar fraction of α,β-ethylenically unsaturated carboxylic acid monomer in the at least one first copolymer (a)(i); and, optionally, a low molecular weight second copolymer (a)(ii) formed of ethylene monomer units and about 3 to about 25 percent by weight α,β-ethylenically unsaturated carboxylic acid monomer units selected from selected from acrylic acid monomer units, methacrylic acid monomer units, and combinations of acrylic acid and methacrylic acid monomer units. The at least one second copolymer (a)(ii) may be included in the thermoplastic polymeric portion in an amount of 0 to about 20 percent by weight based on the combined weight of (a) the first and second copolymers in the thermoplastic polymeric portion. The cover composition comprises the thermoplastic polymeric portion and may also include nonpolymeric materials, for example pigment, filler, and other additives in any combination, including functional additives such as reinforcing chopped fibers, aramid fibers and micropulps, organo-clays to achieve exfoliated nano-platlets, nano-silicas, and so on, which may be used in any combination and which may be present in the cover to further enhance the mechanical properties, such as stiffness, scuff resistance, or wear resistance.

[0035] The at least one high molecular weight first copolymer (a)(i) and the at least one high molecular weight dipolymer (b) each have a weight average molecular weight of from about 80,000 to about 500,000 daltons. The low molecular weight at least one second copolymer (a)(ii) has a weight average molecular weight of from about 2000 to about 30,000 daltons.

[0036] 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 core and the cover, a three-piece ball with a core, an intermediate layer, and the cover, as well as balls with five or more pieces that include the disclosed cover.
The cover 18 defines an outermost structural layer of the ball 10 and generally 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 all layers share a common geometric center.

The golf ball cover is made from a thermoplastic, ionomeric composition. The thermoplastic polymeric portion of the golf ball cover consists essentially of, or consists of, (a) at least one first copolymer (a)(i) and optionally at least one second copolymer (a)(ii) and (b) at least one dipolymer. The component (a) is from about 10 to about 90 percent by weight, based on total weight of (a) and (b).

The component (a) consists of from about 80 to 100 percent by weight, based on a total weight of (a)(i) and (a)(ii), of the at least one first copolymer (a)(i) and from about 0 to about 20 percent by weight, based on a total weight of (a)(i) and (a)(ii), of the at least one second copolymer (a)(ii). The at least one first copolymer (a)(i) consists of ethylene monomer units, from about 5 to about 12 percent by weight of α,β-ethylenically unsaturated carboxylic acid monomer units selected from acrylic acid monomer units, methacrylic acid monomer units, or both acrylic acid and methacrylic acid monomer units, and from about 5 to about 40 percent by weight of alkyl acrylate monomer units, alkyl methacrylate monomer units, or a combination alkyl acrylate monomer units and alkyl methacrylate monomer units. The at least one second copolymer consists of ethylene monomer units and from about 3 to about 25 percent by weight of α,β-ethylenically unsaturated carboxylic acid monomer units selected from acrylic acid monomer units, methacrylic acid monomer units, or both acrylic acid and methacrylic acid monomer units.

The at least one dipolymer consists of ethylene monomer units and acrylic acid monomer units. The molar fraction of acrylic acid monomer units in the at least one dipolymer (b) is within ± about 10% of the molar fraction of α,β-ethylenically unsaturated carboxylic acid monomer units in the at least one first copolymer (a)(i). The molar fraction of α,β-ethylenically unsaturated carboxylic acid monomer units of the first copolymer (a)(i) is the moles of α,β-ethylenically unsaturated carboxylic acid monomer units of all first copolymers (a)(i) divided by the total moles of all constituent monomer units of all first copolymers (a)(i). Similarly, the molar fraction of acrylic acid monomer units of the
dipolymer (b) is the moles of acrylic acid monomer units of all dipolymers (b) divided by the
total moles of all constituent monomer units of all dipolymers (b).

[0041] The first copolymer (a)(i) has a weight average molecular weight of
from about 80,000 to about 500,000 daltons. The second copolymer (a)(ii) has a weight
average molecular weight of from about 2000 to about 30,000 daltons. The dipolymer (b)
has a weight average molecular weight of from about 80,000 to about 500,000 daltons. From
about 30% to about 75% on a molar basis of the combined carboxyl groups of the α,β-
ethylenically unsaturated carboxylic acid monomer units of (a) and the acrylic acid monomer
units of (b) are neutralized with cations selected from the group consisting of magnesium
cations, calcium cations, zinc cations, and combinations thereof.

[0042] The first copolymer has or first copolymers (a)(i) have the α,β-
ethylenically unsaturated carboxylic acid monomer units selected from the group consisting
of acrylic acid monomer units, methacrylic acid monomer units, and combinations of acrylic
acid monomer units and methacrylic acid monomer units present in an amount of from about
5 to about 12 percent by weight based on total first copolymer weight. In one example, the
first copolymer may have from about 5 percent by weight or from about 6 percent by weight
or from about 7 percent by weight or from about 8 percent by weight and up to about 12
percent by weight or up to about 11 percent by weight or up to about 10 percent by weight of
the copolymerized acrylic acid monomer units, methacrylic acid monomer units, or both
acrylic acid and methacrylic acid monomer units. In an example, the first copolymer may
have from about 5 percent by weight to about 11 percent by weight of the α,β-ethylenically
unsaturated carboxylic acid monomer units present. In another example, the first copolymer
may have from about 6 percent by weight to about 11 percent by weight of the α,β-
ethylenically unsaturated carboxylic acid monomer units present. In another example, the
first copolymer may have from about 6 percent by weight to about 10 percent by weight of
the α,β-ethylenically unsaturated carboxylic acid monomer units present. In still another
example, the first copolymer may have from about 7 percent by weight to about 11 percent
by weight of the α,β-ethylenically unsaturated carboxylic acid monomer units present. In yet
another example, the first copolymer may have from about 7 percent by weight to about 10
percent by weight of the α,β-ethylenically unsaturated carboxylic acid monomer units
present. Still further, the first copolymer may have from about 8 percent by weight to about
10 percent by weight or from about 8 to about 9 percent by weight of the α,β-ethylenically
unsaturated carboxylic acid monomer units present.

[0043] The copolymerized α,β-ethylenically unsaturated carboxylic acid
monomer units of the first copolymer may be all acrylic acid monomer units, all methacrylic
acid monomer units, or a combination of acrylic acid monomer units and methacrylic acid monomer units. When a combination of acrylic acid monomer units and methacrylic acid monomer units are used, the at least one first copolymer may be one first copolymer or a plurality of first copolymers that contain both acrylic acid monomer units and methacrylic acid monomer units, optionally in addition to one or more first copolymers that contain only acrylic acid monomer units or that contain only methacrylic acid monomer units. Alternatively, when a combination of acrylic acid monomer units and methacrylic acid monomer units are present in the at least one first copolymer (a)(i), the cover's thermoplastic polymeric portion may contain a plurality of first copolymers (a)(i), at least one of which contains only acrylic acid monomer units and at least one of which contains only methacrylic acid monomer units.

[0044] The first copolymer (a)(i) includes or first copolymers (a)(i) include from about 5 to about 40 percent by weight of alkyl acrylate monomer units, alkyl methacrylate monomer units, or both alkyl acrylate monomer units and alkyl methacrylate monomer units monomer units. Nonlimiting examples of suitable alkyl acrylates and alkyl methacrylates that may be copolymerized with the ethylene and α,β-ethylenically unsaturated carboxylic acid to form the first copolymer (a)(i) include alkyl esters of acrylic acid and methacrylic acid in which the alkyl group has from one to about 8 carbon atoms. In various embodiments, the alkyl group of the ester may have from 2 to 8 carbon atoms. In other examples, the alkyl group of the ester may have from 2 to 7 carbon atoms. In still other examples, the alkyl group of the ester may have from 2 to 6 carbon atoms. The first copolymer (a)(i) may contain the alkyl acrylate monomer units and alkyl methacrylate monomer units in any combination and, for each combination, in any proportion of the various alkyl acrylate monomer units and alkyl methacrylate monomer units. Yet further, the alkyl group of the ester may have 3 or 4 or 5 or 6 carbon atoms, for instance the alkyl group of the ester may have 3 or 4 carbon atoms. Nonlimiting examples of suitable alkyl acrylates and alkyl methacrylates that may be polymerized to form copolymerized units of the first copolymer (a)(i) are methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, isopropyl acrylate, isopropyl methacrylate, butyl acrylate, butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, sec-butyl acrylate, sec-butyl methacrylate, tert-butyl acrylate, tert-butyl methacrylate, hexyl acrylate, hexyl methacrylate, 2-ethylhexyl acrylate, and 2-ethylhexyl methacrylate, which may be used in any combination.

[0045] The alkyl acrylate monomer units, alkyl methacrylate monomer units, or both alkyl acrylate monomer units and alkyl methacrylate monomer units may be present
in a weight percentage of the first copolymer (a)(i) in a range of from about 5 or about 6 or about 7 or about 8 or about 10 or about 12 or about 15 or about 20 weight percent of the of the first copolymer (a)(i) and an upper limit of about 23 or about 25 or about 30 or about 35 or about 40 weight percent of the first copolymer (a)(i). Particular pairs of lower and upper range limits for the alkyl acrylate, alkyl methacrylate, or both alkyl acrylate monomer units and alkyl methacrylate monomer units that may be mentioned include from about 10 weight percent to about 40 weight percent, from about 5 weight percent to about 35 weight percent, from about 10 weight percent to about 35 weight percent, from about 15 weight percent to about 40 weight percent, from about 15 weight percent to about 35 weight percent, and from about 20 weight percent to about 35 weight percent, of the first copolymer (a)(i).

[0046] Nonlimiting specific examples of the at least one first copolymers (a)(i) include first 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/acrylic acid/hexyl acrylate, ethylene/methacrylic acid/hexyl acrylate, ethylene/acrylic acid/hexyl methacrylate, ethylene/methacrylic acid/hexyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl acrylate, and ethylene/methacrylic acid/methyl methacrylate. In various embodiment, the at least one first copolymer (a)(i) may be one or more of ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/n-butyl acrylate, ethylene/methacrylic acid/isobutyl acrylate, ethylene/acrylic acid/isobutyl acrylate.

[0047] The first copolymer (a)(i) has or first copolymers (a)(i) each has a weight average molecular weight of from about 80,000 daltons or from about 100,000 daltons or from about 120,000 daltons or from about 150,000 daltons to about 300,000 daltons or to about 350,000 daltons or to about 400,000 daltons or to about 450,000 daltons or to about 500,000 daltons. In various embodiments, the first copolymer (a)(i) can have or first copolymers (a)(i) each can have a weight average molecular weight of from about 80,000 daltons to about 450,000 daltons or from about 100,000 daltons to about 450,000 daltons or from about 120,000 daltons to about 400,000 daltons or from about 150,000 daltons to about 350,000 daltons. It or they each can have a polydispersity (Mw/Mn) of from about 1 to about 15 or a polydispersity of from about 1 to about 10 or a polydispersity of from about 1 to about 5 or a polydispersity of from about 1 to about 3.

[0048] The second copolymer or copolymers (a)(ii) may have the α,β-ethylenically unsaturated carboxylic acid monomer units selected from the group consisting of acrylic acid monomer units, methacrylic acid monomer units, and combinations of acrylic acid monomer units and methacrylic acid monomer units present in an amount in a range
having a lower limit of about 3 or about 4 or about 5 or about 6 or about 7 or about 8 or
about 9 or about 10 weight percent and an upper limit of about 25 or about 23 or about 20 or
about 18 or about 16 weight percent based on the total weight of the second copolymer
(a)(ii). For example, the second copolymer or copolymers (a)(ii) may have the α,β-
ethylenically unsaturated carboxylic acid monomer units present in an amount of from about
3 to about 25 weight percent or present in an amount of from about 5 to about 20 weight
percent. In other embodiments, the second copolymer or copolymers (a)(ii) may have the
α,β-ethylenically unsaturated carboxylic acid monomer units present in an amount of from
about 7 to about 18 weight percent or present in an amount of from about 8 to about 18
weight percent.

[0049] The copolymerized α,β-ethylenically unsaturated carboxylic acid
monomer units of the second copolymer (a)(ii) may be all acrylic acid monomer units, all
methacrylic acid monomer units, or a combination of acrylic acid monomer units and
methacrylic acid monomer units. When a combination of acrylic acid monomer units and
methacrylic acid monomer units are used, the at least one second copolymer (a)(ii) may be
one second copolymer (a)(ii) or a plurality of second copolymers (a)(ii) that contain both
acrylic acid monomer units and methacrylic acid monomer units, optionally in addition to one
or more second copolymers (a)(ii) that contain only acrylic acid monomer units or that
contain only methacrylic acid monomer units. Alternatively, when a combination of acrylic
acid monomer units and methacrylic acid monomer units are present in the at least one
second copolymer (a)(ii), the cover's thermoplastic polymeric portion may contain a plurality
of second copolymers (a)(ii), at least one of which contains only acrylic acid monomer units
and at least one of which contains only methacrylic acid monomer units.

[0050] The amount of acrylic acid monomer units, methacrylic acid monomer
units, or both acrylic acid monomer units and methacrylic acid monomer units in the second
copolymer or copolymers (a)(ii) is independent of the amount of acrylic acid monomer units,
methacrylic acid monomer units, or both acrylic acid monomer units and methacrylic acid
monomer units in the first copolymer or first copolymers (a)(i) and also independent of the
amount of acrylic acid monomer units in the dipolymer or dipolymers (b).

[0051] The second copolymer (a)(ii) has or the second copolymers (a)(ii) each
has a weight average molecular weight of from about 2000 daltons or from about 3000
daltons or from about 5000 daltons or from about 8000 daltons to about 30,000 daltons or to
about 28,000 daltons or to about 25,000 daltons or to about 20,000 daltons or to about
18,000 daltons. In various embodiments, the second copolymer (a)(ii) has or each of the
second copolymers (a)(ii) has a weight average molecular weight of from about 2000 daltons
to about 30,000 daltons or from about 5000 daltons to about 25,000 daltons or from about 10,000 daltons to about 25,000 daltons or from about 10,000 daltons to about 20,000 daltons.

It or they each can have a polydispersity (Mw/Mn) of from about 1 to about 15 or a polydispersity of from about 1 to about 10 or a polydispersity of from about 1 to about 5 or a polydispersity of from about 1 to about 3.

[0052] The second copolymer (a)(ii) is or second copolymers (a)(ii) are optional components and thus are not required for the cover's polymeric portion, but when present the second copolymer (a)(ii) is or second copolymers (a)(ii) are present in a range of from a finite amount or from about 1 percent by weight or from about 2 percent by weight or from about 3 percent by weight or from about 5 percent by weight or from about 7 percent by weight or from about 10 percent by weight up to about 20 percent by weight or up to about 18 percent by weight or up to about 16 percent by weight or up to about 15 percent by weight, based in each case on the sum of the weights of (a)(i) and (a)(ii). For example, the second copolymer (a)(ii) or second copolymers (a)(ii) may be present in a range of from about 1 percent by weight to about 20 percent by weight, based on the sum of the weights of (a)(i) and (a)(ii). In other examples, the second copolymer (a)(ii) or second copolymers (a)(ii) may be present in a range of from about 5 percent by weight to about 20 percent by weight or in a range of from about 5 percent by weight to about 15 percent by weight, based on the sum of the weights of (a)(i) and (a)(ii). Conversely, when the second copolymer (a)(ii) is or second copolymers (a)(ii) are included in the cover's polymeric portion, the first copolymer (a)(i) is or first copolymers (a)(i) are collectively present in a range of from about 80 percent by weight or from about 82 percent by weight or from about 84 percent by weight or from about 85 percent by weight up to about 100 percent by weight or up to about 99 percent by weight or up to about 97 percent by weight or up to about 95 percent by weight or up to about 95 percent by weight or up to about 93 percent by weight or up to about 90 percent by weight, based in each case on the sum of the weights of (a)(i) and (a)(ii). For example, the first copolymer (a)(i) or first copolymers (a)(i) may be present in a range of from about 80 percent by weight to about 99 percent by weight, based on the sum of the weights of (a)(i) and (a)(ii). In other examples, the first copolymer (a)(i) or first copolymers (a)(i) may be present in a range of from about 80 percent by weight to about 95 percent by weight or in a range of from about 75 percent by weight to about 95 percent by weight, based on the sum of the weights of (a)(i) and (a)(ii).

[0053] The polymeric portion of the cover also includes at least one dipolymer of ethylene and acrylic acid (b). The molar fraction of acrylic acid monomer units of the at least one dipolymer (b) is within ± about 10% of, or within ± about 8% of, or within ± about 6% of, or within ± about 5% of, or within ± about 4% of, or within ± about 3% of, or within ± about 2% of, or within ± about 1% of, or within ± about 0.5% of.
about 2% of, or within ± about 1% of, or within ± about 0.5% of, or about the same as the molar fraction of α,β-ethylenically unsaturated carboxylic acid monomer units in the at least one first copolymer (a)(i). When there is a plurality of dipolymers (b), the molar fraction of acrylic acid monomer units is the average molar fraction of acrylic acid monomer units for all of the dipolymers (b). That is, it is the moles of all acrylic acid monomer units in all dipolymers (b) divided by the total moles of all the constituent monomer units of all dipolymers (b). Likewise, when there is a plurality of first copolymers (a)(i), the molar fraction of α,β-ethylenically unsaturated carboxylic acid monomer units is the average molar fraction for all of the first copolymers (a)(i), which is the moles of all α,β-ethylenically unsaturated carboxylic acid monomer units in all first copolymers (a)(i) divided by the total moles of all the constituent monomer units of all first copolymers (a)(i).

[0054] The dipolymer (b) has or each of the dipolymers (b) has a weight average molecular weight of from about 80,000 daltons or from about 100,000 daltons or from about 120,000 daltons or from about 150,000 daltons to about 300,000 daltons or to about 350,000 daltons or to about 400,000 daltons or to about 450,000 daltons or to about 500,000 daltons. In various embodiments, the dipolymer (b) has or each of the dipolymers (b) has a weight average molecular weight of from about 80,000 daltons to about 450,000 daltons or from about 100,000 daltons to about 450,000 daltons or from about 120,000 daltons to about 400,000 daltons or from about 150,000 daltons to about 350,000 daltons. It or they each can have a polydispersity (Mw/Mn) of from about 1 to about 1.5 or a polydispersity of from about 1 to about 10 or a polydispersity of from about 1 to about 5 or a polydispersity of from about 1 to about 3. The molecular weight and polydispersity of the dipolymer (b) or of each dipolymer (b) is independent of the molecular weight and polydispersity of the first copolymer (a)(i) or of any of the first copolymers (a)(i).

[0055] The polymeric portion of the cover or composition from which the cover is made has from about 10 percent by weight or from about 15 percent by weight or from about 20 percent by weight or from about 25 percent by weight or from about 30 percent by weight or from about 35 percent by weight or from about 40 percent by weight or from about 45 percent by weight up to about 90 percent by weight or up to about 85 percent by weight or up to about 80 percent by weight or up to about 75 percent by weight or up to about 70 percent by weight or up to about 65 percent by weight or up to about 60 percent by weight or up to about 55 percent by weight of the at least one dipolymer (b) based on the combined weights of components (a) (the first copolymer or first copolymers (a)(i) and, if present, the dipolymer or dipolymers (a)(ii)) and (b) (the at least one dipolymer (b)). While the amount of the at least one dipolymer (b) may be in a range having a lower limit selected
from any of these just given and a higher limit selected from any of these just given, examples of ranges for the amount of the at least one dipolymer (b) are from about 10 percent by weight to about 90 percent by weight or from about 20 percent by weight to about 80 percent by weight or from about 25 percent by weight to about 75 percent by weight or from about 30 percent by weight to about 65 percent by weight, in each case based on the combined weights of components (a) and (b).

[0056] Methods of preparing the at least one first copolymer (a)(i), at least one second copolymer (a)(ii), and at least one dipolymer (b) are known and include, for example continuous polymerization in by use of "co-solvent technology" as described in U.S. Pat. No. 5,028,674, which is incorporated by reference, as well as batch polymerization in solution or neat (particularly for the low molecular weight second copolymer (a)(ii)) or by emulsion polymerization (particularly for the high molecular weight polymers). Polymerization may be carried out using any convenient free radical initiator or initiators, for example.

[0057] From about 30% to about 75% on a molar basis of the combined carboxyl groups of the α,β-ethylenically unsaturated carboxylic acid monomer units of components (a) and of the acrylic acid monomer units of (b) (that is, the at least one first copolymer (a)(i), the at least one second copolymer (a)(ii) (if present) and the at least one dipolymer (b)) are neutralized with cations selected from the group consisting of magnesium cations, calcium cations, zinc cations, and combinations thereof. In various embodiments, the neutralizing cations are selected from magnesium cations, calcium cations, and combinations thereof. In certain embodiments, the neutralizing cations are calcium cations.

[0058] Ionic compounds that may be used as sources of the neutralizing cations include formates, acetates, nitrates, carbonates, hydrogen carbonates, oxides, hydroxides or alkoxides. The amount of ionic compound capable of neutralizing a certain number of carboxyl groups (referred to herein as "% nominal neutralization" or "nominally neutralized") may be determined by simple stoichiometric principles. When an amount of cation sufficient to neutralize a target amount of carboxyl groups is made available in a melt of first copolymer (a)(i) or second copolymer (a)(ii) or component (a) or component (b) or combination of components (a) and (b) of the thermoplastic portion, it is assumed that, in aggregate, the indicated level of nominal neutralization is achieved.

[0059] The at least one copolymer (a)(i), at least one copolymer (a)(ii), and at least one dipolymer (b) can be neutralized separately with different cations or the same cation to the same or different degrees of neutralization, and then subsequently melt blended into the final composition at the desired proportion and further neutralized if desired. The range of neutralization may on a molar basis for the at least one copolymer (a)(i), at least one
copolymers (a)(ii), and at least one dipolymer (b) may be independent from the range of neutralization of from 35% to 75% on a molar basis, for the combination of the at least one copolymer (a)(i), at least one copolymer (a)(ii), and at least one dipolymer (b) in the cover composition. For example, the range of neutralization can be from 35% to 75% on a molar basis, for the at least one copolymer (a)(i), at least one copolymer (a)(ii), and at least one dipolymer (b) independently and for the combination of components the at least one copolymer (a)(i), at least one copolymer (a)(ii), and at least one dipolymer (b) in the cover composition. In another example, the range of neutralization can be from 40% to 75% on a molar basis, for the at least one copolymer (a)(i), at least one copolymer (a)(ii), and at least one dipolymer (b) independently and for the combination of components (a) and (b) in the cover composition. The range of neutralization of the at least one first copolymer (a)(i) and the at least one second copolymer (a)(ii) may be independent of the range of neutralization of the component (a) that they form together, and the component (a) may be further neutralized after the at least one first copolymer (a)(i) and the at least one second copolymer (a)(ii) are combined or the combination of components (a) and (b) may be further neutralized after (a) and (b) are combined.

[0060] The at least one first copolymer (a)(i), the at least one second copolymer (a)(ii), and the at least one dipolymer (b) may combined in any order, either before or after being independently neutralized or partially neutralized.

[0061] In one example, the non-neutralized high molecular weight first copolymer or first copolymers (a)(i) and low molecular weight copolymer (a)(ii) (if any) of (a) are melt-blended and then neutralized so that desired higher or full neutralization may be achieved in one step. The unneutralized or neutralized dipolymer or dipolymer (b) may then be added, and optionally the resulting mixture may be further neutralized.

[0062] In any case, neutralization may be effected by treating the polymers with a basic compound such as any of those already mentioned. The basic compound(s) may be added neat to the polymer(s) or they may be premixed with a polymeric material, such one of the acid polymers of (a) or (b), for example with a second copolymer (a)(ii), to form a "masterbatch" that may be added to the remaining copolymers to form the polymeric portion or cover composition.
Another example involves melt blending the pre-neutralized component (a) and component (b) with the same or different neutralizing agents to the same or different degrees of neutralization at the desired blend ratios to achieve the cover compositions.

In addition to the thermoplastic polymeric portion, the cover compositions may further comprise small amounts of optional materials commonly used and well known in the polymer art, such as conventional additives including reinforcing chopped fibers, aramide fibers and micropulps, organo-clays to achieve exfoliated nano-plates, nanosilicas, or other fillers to further enhance the mechanical properties, such as stiffness, scuff resistance, wear resistance; plasticizers; stabilizers including viscosity stabilizers and hydrolytic stabilizers, primary and secondary antioxidants such as for example IRGANOX™1010, and ultraviolet light absorbers; anti-static agents; dyes, pigments such as titanium dioxide, or other coloring agents, and optical brighteners; fire-retardants; lubricants, processing aids, slip additives, antblock agents such as silica or talc, release agents; and so on, which may be used in any combination.

These conventional additives may be present in the cover in quantities that are generally from 0.01 to 15 weight %. The conventional additives may be present in quantities of from 0.01 to 5 weight % based on the total weight of the composition. The conventional additives may be present in quantities of from 0.01 to 10 weight %, based on the total weight of the cover. The quantity of conventional additives is selected to not detract from the basic and novel characteristics of the cover and to not significantly adversely affect the performance of the cover of the golf ball.

The incorporation of these optional materials into the cover 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.

The thermoplastic composition including the polymeric portion for the cover may be formulated with a pigment, such as a yellow or white pigment, and in particular a white pigment such as titanium dioxide or zinc oxide, an aluminum pigment, or a white pearlescent pigment such as titanium dioxide-coated mica pigments. White, silver metallic, and white pearl colors provide dyed second colors that are truest to the dye selected, but other first colors, particularly light colors such as a light yellow, can be used to create a different color with the dye. Generally, dark or intense first colors are avoided, but pigments of many colors may be used to provide light colors or for tinting, and special effect pigments may also be used as desired. Examples of other pigments that could be used include inorganic pigment such as red iron oxide, transparent red iron oxide, chromium oxide green, ferric ammonium
ferrocyanide (Prussian blue), and ultramarine; organic pigments such as metallized and non-
metallized azo reds, quinacridone reds and violets, perylene reds, copper phthalocyanine
blues and greens, carbazole violet, monoarylide and diarylide yellows, benzimidazolone
yellows, tolyl orange, and naphthol orange; and flake pigments such as copper flake
pigments, zinc flake pigments, stainless steel flake pigments, and bronze flake pigments, and
iron oxide-coated mica pigments; and fluorescent or phosphorescent pigments such as zinc
sulfide, cadmium sulfide, and metal aluminate phosphorescent pigments. Generally titanium
dioxide is used as a white pigment, for example in amounts of from about 0.5 parts by weight
or 1 part by weight to about 8 parts by weight or 10 parts by weight based on 100 parts by
weight of resin. In various embodiments, a white-colored cover may be tinted with a small
amount of blue pigment or brightener.

[0068] The cover may also contain one or more customary additives such as
fillers, dispersants, hindered amine light stabilizers such as piperidines and oxanilides,
ultraviolet light absorbers such as benzotriazoles, triazines, and hindered phenols,
antioxidants such as phenols, phosphites, and hydrazides, plasticizers, defoaming agents,
processing aids, surfactants, fluorescent materials and fluorescent brighteners, and so on.

[0069] The cover can include a filler such as, but not limited to, chopped
fibers, aramide fibers and micropulps, other pulps, organo-clays having exfoliated nano-
platlets, nano-silicas, other nano-fillers, clay, talc, asbestos, graphite, glass, mica, barium
sulfate, aluminum hydroxide, calcium carbonate, magnesium carbonate, and other metal
carbonates, zinc sulfide, calcium metasilicate and other 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 zinc oxide, magnesium oxide, 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.

[0070] Fillers may be used to adjust the specific gravity, modulus, and other
physical properties of the cover. The total amount of the filler may be from about 0.5 to
about 30 percent by weight of the cover composition. Wetting or dispersing additives may be
used to more effectively disperse the pigments and particulate fillers. Generally, the
additives will be present in the composition in an amount between about 1 and about 25
weight percent based on the total weight of the cover composition depending upon the desired properties.

[0071] The cover may be injection molded or compression molded around the core and any intermediate layers. The injection molding temperature may generally be in a range of from 150 to 250 °C. 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.

[0072] 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%.

[0073] Typically, the cover may have a thickness of from about 0.5 mm or from about 1 mm or from about 1.5 mm up to about 2 mm or up to about 2.5 mm or up to about 3 mm, although golf ball may also be made with covers having a thickness of less than about 0.5 mm or up to about 5 mm.

[0074] One or more coating layers may be applied to the cover of the golf ball, and these may be pigmented or clear, thermoplastic or thermoset.

[0075] In addition to having a cover, the golf ball may have any known construction. Examples include a two-piece golf ball comprising a unitary core and a cover around the core; a three-piece ball comprising a core, an intermediate layer, and a cover layer; or a multi-layer golf ball comprising more than one intermediate layer between core and cover. The core of the golf ball may be solid, semi-solid (e.g., paste or gel), hollow, or filled with a fluid or powder in a one-piece or multi-piece construction. As used in
describing the core, a fluid may be a liquid, paste, gel, gas, or some combination of these. The core and any intermediate layer or layers may be made from known golf ball materials, including thermoset elastomers, thermoplastic elastomers, and ionomers. Nonlimiting examples of thermoset elastomers include natural rubber and synthetic rubbers such as styrene butadiene rubber, polybutadiene rubber, polyisoprene rubber, styrene-butadiene rubber (SBR), and ethylene-propylene-diene first copolymer (EPDM). In various embodiments, a high cis-polybutadiene crosslinked with a diacrylate such as zinc diacrylate is used for a core or intermediate layer. The high cis-polybutadiene can comprise 40-100% by weight of the cis form. The high cis-polybutadiene can comprise 70-100% by weight of the cis form. The high cis-polybutadiene can comprise 90-100% by weight of the cis form. Nonlimiting examples of suitable thermoplastic elastomers are metallocene-catalyzed block copolymers of ethylene and cc-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-cobutylene-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. The core and each intermediate layer may include fillers or other customary additives. The golf ball cores may be formed using any conventional techniques.

The golf ball can be manufactured so as to conform with the Rules of Golf for competitive play with a ball diameter which is of a size that will not pass through a ring having an inside diameter of 42.672 mm, but is not more than 42.80 mm, and to a weight of generally from 45.0 to 45.93 g. The cover made of the disclosed composition has excellent scuff resistance while providing a desirable hardness and flex modulus.

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 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.
What is claimed is:

1. A golf ball having a core and a cover, wherein the cover comprises a thermoplastic polymeric portion consisting essentially of

   (a) (i) at least one first copolymer that has a weight average molecular weight of from about 80,000 to about 500,000 daltons and that consists of ethylene monomer units, from about 5 to about 12 percent by weight of \( \alpha, \beta \)-ethylenically unsaturated carboxylic acid monomer units selected from the group consisting of acrylic acid monomer units, methacrylic acid monomer units, and combinations thereof, and from about 5 to about 40 percent by weight of at least one member selected from the group consisting of alkyl acrylate monomer units, alkyl methacrylate monomer units, and combinations thereof;

   (ii) at least one second copolymer that has a weight average molecular weight of from about 2000 to about 30,000 daltons and that consists of ethylene monomer units and from about 3 to about 25 percent by weight of \( \alpha, \beta \)-ethylenically unsaturated carboxylic acid monomer units selected from the group consisting of acrylic acid monomer units, methacrylic acid monomer units, and combinations thereof,

   wherein (a)(i) is from about 80 to 100 percent by weight of the sum of the weights of (a)(i) and (a)(ii) and (a)(ii) is from 0 to about 20 percent by weight of the sum of the weights of (a)(i) and (a)(ii); and

   (b) at least one dipolymer that has a weight average molecular weight of from about 80,000 to about 500,000 daltons and that consists of ethylene monomer units and acrylic acid monomer units, wherein the at least one dipolymer has a molar fraction of the acrylic acid monomer units that is within ± about 10% of a molar fraction of the \( \alpha, \beta \)-ethylenically unsaturated carboxylic acid monomer units of the at least one first copolymer (a)(i);

   wherein (b) is from about 10 to about 90 percent by weight of a combined weight of (a) and (b), and

   wherein from about 30% to about 75% on a molar basis of total acid groups of (a) and (b) are neutralized with cations selected from the group consisting of magnesium cations, calcium cations, zinc cations, and combinations thereof.

2. A golf ball according to claim 1, wherein the at least one first copolymer (a)(i) has from about 8 to about 12 percent by weight of \( \alpha, \beta \)-ethylenically unsaturated carboxylic acid monomer units.
3. A golf ball according to claim 1 or claim 2, wherein the at least one dipolymer (b) has a molar fraction of acrylic acid monomer units within ± about 5% of the molar fraction of α,β-ethylenically unsaturated carboxylic acid monomer units of the at least one first copolymer (a)(i).

4. A golf ball according to any one of claims 1 to 3, wherein the at least one dipolymer (b) has a molar fraction of acrylic acid monomer units within ± about 3% of the molar fraction of α,β-ethylenically unsaturated carboxylic acid monomer units of the at least one first copolymer (a)(i).

5. A golf ball according to any one of claims 1 to 4, wherein the weight average molecular weight of the at least one first copolymer (a)(i) is from about 200,000 to about 400,000 daltons and the weight average molecular weight of the at least one dipolymer (b) is from about 200,000 to about 400,000 daltons.

6. A golf ball according to any one of claims 1 to 5, wherein from about 50% to about 100% on a molar basis of the neutralizing cations are selected from the group consisting of magnesium cations, calcium cations, and combinations thereof.

7. A golf ball according to any one of claims 1 to 6, wherein the at least one member of (a)(i) comprises n-butyl acrylate monomer units.

8. A golf ball according to any one of claims 1 to 7, wherein the α,β-ethylenically unsaturated carboxylic acid monomer units of the at least one first copolymer (a)(i) are acrylic acid monomer units.

9. A golf ball according to any one of claims 1 to 8, wherein the α,β-ethylenically unsaturated carboxylic acid monomer units of the at least one second copolymer (a)(ii) are acrylic acid monomer units.

10. A golf ball according to any one of claims 1 to 8, wherein (a)(i) is 100 percent by weight and (a)(ii) is 0 percent by weight of the sum of the weights of (a)(i) and (a)(ii).

11. A golf ball according to any one of claims 1 to 10, wherein from about 50% to about
100% on a molar basis of the neutralizing cations are calcium cations.

12. A golf ball according to claim 11, wherein 100% on a molar basis of the neutralizing cations are calcium cations.

13. A golf ball according to any one of claims 1 to 10, wherein the cover has a thickness of from about 1 mm to about 3 mm.

14. A method of manufacturing a golf ball having a core and a cover, comprising:

   forming the cover around the core from a thermoplastic polymeric portion consisting essentially of

   (a) (i) at least one first copolymer that has a weight average molecular weight of from about 80,000 to about 500,000 daltons and that consists of ethylene monomer units, from about 5 to about 12 percent by weight of α,β-ethylenically unsaturated carboxylic acid monomer units selected from the group consisting of acrylic acid monomer units, methacrylic acid monomer units, and combinations thereof, and from about 5 to about 40 percent by weight of at least one member selected from the group consisting of alkyl acrylate monomer units, alkyl methacrylate monomer units, and combinations thereof;

   (ii) at least one second copolymer that has a weight average molecular weight of from about 2000 to about 30,000 daltons and that consists of ethylene monomer units and from about 3 to about 25 percent by weight of α,β-ethylenically unsaturated carboxylic acid monomer units selected from the group consisting of acrylic acid monomer units, methacrylic acid monomer units, and combinations thereof,

   wherein (a)(i) is from about 80 to 100 percent by weight of the sum of the weights of (a)(i) and (a)(ii) and (a)(ii) is from 0 to about 20 percent by weight of the sum of the weights of (a)(i) and (a)(ii); and

   (b) at least one dipolymer that has a weight average molecular weight of from about 80,000 to about 500,000 daltons and that consists of ethylene monomer units and acrylic acid monomer units, wherein the at least one dipolymer has a molar fraction of the acrylic acid monomer units that is within ± about 10% of a molar fraction of the α,β-ethylenically unsaturated carboxylic acid monomer units of the at least one first copolymer (a)(i);

   wherein (b) is from about 10 to about 90 percent by weight of a combined weight of (a) and (b), and

   wherein from about 30% to about 75% on a molar basis of total acid groups of (a) and
(b) are neutralized with cations selected from the group consisting of magnesium cations, calcium cations, zinc cations, and combinations thereof.

15. A method according to claim 14, wherein the step of forming the cover comprises forming the cover to have a thickness of from about 1 mm to about 3 mm.
**INTERNATIONAL SEARCH REPORT**

**INTERNATIONAL APPLICATION No:**
PCT/US2015/023895

**A. CLASSIFICATION OF SUBJECT MATTER**

| INV. | A63B37/00 | C08L23/08 | C08L23/04 |

**ADD.**

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

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

- A63B
- 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**

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**Date of the actual completion of the international search**

18 June 2015

**Date of mailing of the international search report**

29/06/2015

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