1. GOLF BALL MADE FROM A VULCANIZED ELASTOMER COMPOSITION

Alvon R. Cox, Ashland, Ohio, assignor to Abbott Laboratories, Chicago, Ill., a corporation of Illinois
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U.S. Cl. 273—218
8 Claims

ABSTRACT OF THE DISCLOSURE

A golf ball made from a unitary solid elastomer prepared by vulcanizing a composition consisting essentially of highly resilient polybutadiene elastomer, trimethyl propane trimethacrylate, a white pigment, a filler material, and a cross-linking agent such as dicumyl peroxide.

This application is a continuation-in-part of my own prior application Ser. No. 317,052 filed Oct. 17, 1963, now abandoned.

The present invention relates to golf balls, and to new and improved compositions for forming a golf ball, which ball is made from a unitary elastomer body having a substantially uniform composition throughout.

At the present time, all high quality balls are made from several different components which usually include a center, some type of a rubber or elastomer strip or thread that is wound around the center and completely encloses the center, and a finish cover that is molded as an integral unit around the wrapped center of the ball. Some efforts have been made heretofore to provide a unitary or homogeneous type of a golf ball but all of such previous efforts have only provided, insofar as I am aware, a low quality ball having relatively poor properties.

It is relatively well known that golf balls are subjected to very severe stresses when used. Thus one test report, for example, has indicated that a golf club head may be moving at a speed approximately 160 ft. per second when it strikes the ball, and that the ball, for a good drive, for example, would leave the club head after momentary impact therewith at a speed of approximately 170 miles per hour. The club head has been measured to be in contact with the golf ball for approximately .0005 second and the golf ball is believed to absorb energy at the rate of about 300 horsepower in the brief contact between the club head and ball. The ball may have a spin of as much as 3500 to 4000 r.p.m. or more imparted thereto at the moment of impact, and the club is believed to exert as much as a ¼ ton impact on the ball when it is struck.

In all events, high quality golf balls as in use today are made of high standard and costly materials and forming operations used to make and assemble the centers, windings, and covers thereof. These balls have specified limits as to their sizes and weights, which limits must be strictly complied with if the ball is to have approval of the governing bodies in golf play, such as United States Golf Association. Furthermore, all good golfers recognize quality balls in most instances by the very pleasant sounding "click" that is obtained when a golf ball is properly struck by a club, such as a driver, and for acceptance of a new ball, it must have a sound comparable to that of relatively expensive, high quality balls of previously known construction.

Therefore, it is the general object of the present invention to provide a new and improved high quality, unitary golf ball of a substantially uniform composition throughout, which golf ball is primarily made from highly resilient polybutadiene rubber elastomers having a methacrylate monomer included therein.

A further object of the invention is to provide a new and improved composition for use in making integral or unitary types of golf balls therefrom and where the composition includes polybutadiene elastomer having an appreciable cis configuration double bond content, trimethyl propane trimethacrylate, and a peroxide curing agent therein.

A further object of the invention is to provide a unitary substantially homogeneous composition golf ball that includes a highly resilient polybutadiene rubber elastomer and which ball has good compression characteristics, a relatively high durometer, a high rebound characteristic, and which has a "click" sound very comparable to that of relatively expensive high quality balls in use today and made from centers, separate windings and molded covers formed integrally around the wrapped ball center.

A further object of the invention is to provide a new and improved golf ball of a unitary construction throughout and which golf ball has high resistance to cutting or marring of the periphery of the golf ball, and which ball has high quality characteristics of play when in use.

The foregoing and other objects or advantages of the invention will be made more apparent as the specification proceeds.

The present invention, in one embodiment thereof, relates to the provision of a golf ball made from a unitary, solid, elastomer made by vulcanization of a composition consisting essentially of the following ingredients in substantially the ratios stated: polybutadiene rubber about 100 parts, trimethyl propane trimethacrylate about 20 to 70 parts, a peroxide curing agent about 0.5 to 10 parts, a finely divided reinforcing pigment about 20 to 60 parts, and a white pigment about 2 to 15 parts, as maximum ranges of the golf ball composition.

In making the new and improved golf ball of the invention, the ball is made primarily from an elastomer comprising 1,4-polybutadiene rubber, which in the compositions stated hereinafter will be used normally as including such elastomer in about 100 parts by weight and the remaining ingredients of the composition and ball produced then can be varied within predetermined limits set forth in relation to this basic elastomer mass. A methacrylate monomer is used between about 20 to 70 parts by weight preferably in the more limited ranges of 25 to 55 parts, and specifically the monomer or ester SR350 which is trimethyl propane trimethacrylate is used.

Cis-type polybutadiene rubber, or elastomer used in practice of the invention is a highly resilient polybutadiene rubber made in a solution polymerization process usually using a stereo-specific catalyst system.

Patents referring to processes for providing synthetic polymers of the type for use with the present invention include British Patent No. 827,365, U.S. Patent No. 3,178,402, and Belgium Patents 551,851; 573,680 and 575,671.

Yet other discussions on rubbers of the general type for use in practice of the invention are found in a paper entitled, "Diene Rubber: A Linear Polybutadiene," which was given at the International Congress sponsored by the German Rubber Society on Oct. 5, 1960, in West Berlin, Germany, which paper was prepared by Glen Alliger, V. L. Johnson, and L. E. Forman, and as an article starting on page 276 of the March, 1961, issue of "Rubber and Plastics Age."

These cis-types of polybutadienes may have some appreciable variation in the number of double bonds in the polymer molecule arranged in the cis configuration and such double bond arrangement usually predominates in these elastomers and with this cis-type configuration being present usually in from about 50% to 60% up to 90% or more. However, some of the polybutadiene elastomers of this general type may have a predominantly trans-type of
3,502,338

double bond configuration and be useful in the practice of the present invention as long as they have, for example, at least about 90% cis. This variable can occur out of 100 double bonds. One commercial elastomer which has been used in practice of the invention is termed Cis-4 rubber and is generally described in U.S. Patent No. 3,178,402. The elastomers may have a small amount such as up to 2 or 3% of 1-2 configuration present therein.

The composition also includes a cross-linking agent in the form of a peroxide, particularly the material DiCup 40C which comprises dicumyl peroxide. This material can be used in the range of from about 0.5 to 10 parts by weight and preferably in the range of about 2 to 8 parts for best results and this substance comprises about 40% active material. Other peroxides or peroxynitrates or PEROXYS may be used in practice of the invention for the dicumyl peroxide would be 2,4-dichloro-benzyl peroxide (50% mix with 50% inert filler); 2,5-dimethyl-2,5-di-t-butyl-peroxide) hexane 45% mix with 55% inert filler; or 2,5 di-methyl-2,5-di-t-butyl-peroxide hexane 3 (43% strength with 57% inert filler), or 90% strength with 10% inert filler.

A finely divided reinforcing pigment, in this instance preferably a white, hydrated silica powder such as HiSil 233 is used in or, its equivalent, may be used in from about 20 to 60 parts by weight and preferably in the composition between about 30 to 45 parts by weight. With increasing amounts of the HiSil 233 being used in the range stated, it provides higher compression and hardness in the resultant golf ball but lowers the rebound characteristics of the ball. HiSil 233 is a precipitated hydrated silica of very fine ultimate particle size and it comprises about 89.2% of silicon dioxide and small amounts of other materials. It has a particle size of approximately 0.002 microns.

While one particular type of hydrated silica has been referred to in forming the improved golf ball composition of the invention, various other known types of fillers, preferably white, can be used in making the composition of the invention so that other type of silicas, such as Silene EF, can be used, while wood filler, barytes, and equivalents can be used in making the composition of the invention. The fillers used are conventional and aid in weight control and strength of bond. Usually the smaller the particle size, the easier it is to process and disperse the filler with the batch and the more effective the filler is for a given total weight.

Another suitable filler includes Dixie Clay which is an inert hard kaolin clay. Silene EF is a hydrated silicate comprising about 65% silica, about 19.5% lime, small amounts of other oxides and salt and the remainder water of hydration. The fillers preferably are of a size to pass through U.S. Standard screen size, No. 325, and some are fine enough to pass through screen size No. 400. The fillers may be used individually or two or more fillers may be used in combination within the ranges stated.

One good method of adjusting the weight of the molded product is to vary the amount of titanium dioxide used. Some size variations may be compensated for by the painting or finishing of the balls.

When increased amounts of the acrylates are used, the resultant golf ball produced tends to have higher compression and hardness and variation in the amount of such material used within the range stated does not appear to reduce the rebound characteristics of the ball obtained more than a few percent.

To aid in improving the color of the ball, and to improve its characteristics in general, appreciable quantities of titanium dioxide are used in the composition, usually from about 2 to 15 parts by weight of this material being suitable but with from about 4 to about 10 parts being preferred. Hence, the amount of white pigment used can be considered to have a range of from about 22 to about 75 parts by weight and the amount of HiSil or equivalent and titanium dioxide used can vary within such range.

Specifically, a very satisfactory golf ball has been produced from the composition consisting essentially of 1.4 polybutadiene about 100 parts by weight, trimethyl propane trimethacrylate about 55 parts by weight, titanium dioxide about 15.0 parts by weight, HiSil about 30 parts by weight, and dicumyl peroxide about 2.5 parts by weight. This golf ball produced from the above formula had a compression of 86 under the standard United States Golf Association test, and had a durometer of 58 on the Shore D scale, had a rebound of 73 inches out of a 100 inch drop, and had a "click" that was very good and comparable to that of relatively expensive, or costly quality golf balls in use today and made from a separate center, winding, and cover. In this golf ball composition, a blue color or pigment material, such as ultramarine blue, may be added to .4 part by weight. This aids in improving the whiteness of the resultant products.

In some instances, it is possible to use the golf ball of the invention without applying any coating or painting thereon, but preferably any suitable paint may be applied to the ball, and be dried thereon, after the ball has been molded. The various ingredients of the elastomer composition of the invention can be mixed in conventional manners, and then be extruded through known equipment into a strip form after which sections of the strip can be severed in the desired quantities and be individually placed in suitable compression molds for production of the finished products. The actual composition set forth hereinabove has been satisfactorily cured in 18 minutes at 320°F.

The golf ball of the invention has had a rebound characteristic that is very comparable to that of high quality balls, and this test usually is performed by dropping the ball onto a hard rebound surface, such as a marble plate or block, and the golf ball when used or tested has a very satisfactory sound pleasing to the ear of the golfer accustomed to high quality golf balls as made and sold today.

EXAMPLE 2

<table>
<thead>
<tr>
<th>Highly resilient polybutadiene</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>SR350</td>
<td>100</td>
</tr>
<tr>
<td>HiSil</td>
<td>45</td>
</tr>
<tr>
<td>DiCup, 40C</td>
<td>30</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.75</td>
</tr>
<tr>
<td>Ultramarine Blue</td>
<td>.01</td>
</tr>
</tbody>
</table>

EXAMPLE 3

<table>
<thead>
<tr>
<th>Polybutadiene elastomer</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene resin</td>
<td>95</td>
</tr>
<tr>
<td>Premix from polybutadiene elastomer, 86 parts:</td>
<td>2.50</td>
</tr>
<tr>
<td>3 parts fatty acid; 3 parts resin 8318; 8 parts naphthenic oil</td>
<td>2.50</td>
</tr>
</tbody>
</table>

Total rubber elastomers. . . . . . . . 100.00

In this example, the polybutadiene, fatty acid, resin 8318, and naphthenic oil are premixed and then 2.50 parts of the premix, modified polybutadiene, are used in the composition as an aid to processing. The modified polybutadiene elastomer of Example 3 includes a suitable fatty acid, such as stearic acid, and about 3 parts of an allylphenol novolak type resin (resin 8318) mixed therewith. The polybutadiene used in Example 3 had a high cis content of over 90%.

Small percentage composition by weight of styrene type resins or elastomers may also be used in the formula used in forming the golf balls of the invention. Such styrene type resins are commercially known today and comprise a co-
polymer of between about 70 to 90% of styrene and from about 30 to 10% butadiene. Such resins are unsaturated and are vulcanizable. They seem to increase the strength and hardness of the finished composition. Also, the resin improves the click of the ball produced. Use of the premix and styrene resin facilitates the processing and molding of the composition. Satisfactory golf balls, meeting U.S.G.A. standards, were made and tested using the formulations of Examples 2 and 3.

One specific reinforcing filler, or pigment, used in practice of the invention is HIsII 233.

Other compositions for practice of the invention include:

<table>
<thead>
<tr>
<th>Material</th>
<th>R58</th>
<th>R66</th>
<th>R69</th>
<th>R81</th>
<th>R94</th>
<th>R94</th>
<th>R113</th>
<th>R113</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cis 4 polybutadiene, 100.0 100.0</td>
<td>55.0</td>
<td>85.0</td>
<td>85.0</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Trimethylol propane</td>
<td>2.50</td>
<td>2.50</td>
<td>2.50</td>
<td>4.40</td>
<td>4.40</td>
<td>4.40</td>
<td>4.40</td>
<td>4.40</td>
</tr>
<tr>
<td>Styrene resin</td>
<td>8.0 300</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Filler (HIsII)</td>
<td>30.0</td>
<td>30.0</td>
<td>30.0</td>
<td>30.0</td>
<td>30.0</td>
<td>30.0</td>
<td>30.0</td>
<td>30.0</td>
</tr>
<tr>
<td>IPP</td>
<td>6.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>DHyp 80C</td>
<td>7.75</td>
<td>7.75</td>
<td>7.75</td>
<td>7.75</td>
<td>7.75</td>
<td>7.75</td>
<td>7.75</td>
<td>7.75</td>
</tr>
<tr>
<td>Color</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The CB—880 material noted in the above examples is a modified cis-type polybutadiene that is a relatively easy processing material. It is the same material as the premix set forth in Example 3 herebefore. The coloring material was ultramarine blue in the above examples and the styrene resin used is as described herebefore. In the CB—880 small quantities of the modifying ingredients are present preferably in about the quantities indicated but changes of about one part plus or minus from the quantities stated for forming the premix can be made and good results are still secured.

Compositions of invention consisting essentially of:

<table>
<thead>
<tr>
<th>Material</th>
<th>Highly resilient polybutadiene</th>
<th>50-100</th>
<th>100</th>
<th>0.66</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>trimethylol propane</td>
<td>20-70</td>
<td>25-35</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>reinforcing pigments (HIsII)</td>
<td>20-40</td>
<td>30-45</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Curing agent (dicumyl peroxide)</td>
<td>3-10</td>
<td>2.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

The rebound characteristics of a golf ball are believed to be improved appreciably when the trimethylol propane trimethacrylate has been used in combination with the dicumyl peroxide. While some variation in the ingredients and compositions stated herebefore are possible, the preferred composition is set forth hereinafter and has given the best results in tests of golf balls produced from these new compositions of the invention.

From the foregoing, it is believed that it will be seen that the objects of the invention have been achieved. While one complete embodiment of the invention has been disclosed herein, it will be appreciated that modification of this particular embodiment of the invention may be resorted to without departing from the scope of the invention as defined in the appended claims.

What is claimed is:

1. A golf ball comprising a spherical unitary, solid elastomer made by vulcanization of the following composition consisting essentially of the following ingredients in the weight ratios stated:
   - a highly resilient polybutadiene rubber having a cis configuration internal double bond of at least 30% of about 100 parts,
   - about 20 to 70 parts of trimethylol propane trimethacrylate,
   - an organic peroxide curing agent about 0.5 to 10 parts, finely divided reinforcing pigment about 20 to 60 parts, and
   - a white pigment about 2 to 15 parts.

2. A golf ball formed from a composition as in claim 1 where said peroxide curing agent is a material from the class consisting of dicumyl peroxide, 2,4 dichlorobenzoyl peroxide, 2,5 dimethyl-2,5-di-(t-buty1-peroxy) hexane 45%, and 2,5 dimethyl-2,5-di-(t-buty1-peroxy) hexane 3 (43% strength with 57% inert filler), or 90% strength with 10% inert filler.

3. A golf ball formed from a composition as in claim 1 where from 25 to 55 parts of trimethylol propane trimethacrylate are used.

4. A golf ball comprising a composition as in claim 1 wherein said highly resilient material including an unvulcanized polybutadiene elastomer includes up to about 3% of 1-2 configuration double bonds therein.

5. A golf ball comprising a spherical unitary, solid elastomer made by vulcanization of the following composition consisting essentially of the following ingredients in the weight ratios stated:
   - a highly resilient conjugated diene elastomer consisting essentially of material having a cis configuration internal double bond above 30% of about 100 parts, about 25 to 55 parts of trimethylol propane trimethacrylate,
   - a peroxide curing agent from the class consisting of dicumyl peroxide, 2,4 dichlorobenzoyl peroxide, 2,5 dimethyl-2,5-di-(t-buty1-peroxy) hexane 45%, and 2,5 dimethyl-2,5-di-(t-buty1-peroxy) hexane 3 (45% strength with 57% inert filler), or 90% strength with 10% inert filler about 2 to 8 parts, finely divided white reinforcing pigment about 30 to 45 parts, and
   - titanium dioxide about 4 to 10 parts.

6. A golf ball comprising a spherical unitary, solid, elastomer made by vulcanization of the composition consisting essentially of the following ingredients in the weight ratios stated:
   - a highly resilient material when vulcanized consisting essentially initially of conjugated polyolefin hydrogenated carbon elastomer having a cis configuration of internal double bonds above about 30% of about 100 parts, about 20 to 70 parts of trimethylol propane trimethacrylate,
   - a peroxide curing agent from the group consisting of dicumyl peroxide, 2,4 dichlorobenzoyl peroxide, 2,5 dimethyl-2,5-di-(t-buty1-peroxy) hexane 45%, and 2,5 dimethyl-2,5-di-(t-buty1-peroxy) hexane 3 (43% strength with 57% inert filler), or 90% strength with 10% inert filler about 0.5 to 10 parts, a finely divided hydrated silica powder about 20 to 60 parts, and
   - from about 2 to about 15 parts of titanium dioxide.

7. A golf ball formed from a composition as in claim 1 where the white pigment comprises titanium dioxide.

8. A golf ball formed from a composition as in claim 1 where the finely divided reinforcing pigments include at least one material from the class consisting of hydrated silica powder, silica, wood filler, barytes, hydrated silicates, and inert hard kaolin clay, and having a particle size to pass through U.S. Standard screen size No. 325.

References Cited

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260—41.5

ALLAN LIEBERMAN, Primary Examiner

260—41.5
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION


Inventor(s) Alvon R. Cox

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 16, "4 part" should read -- .04 part -- .

Signed and sealed this 18th day of August 1970.

(SEAL)
Attest:
EDWARD M. FLETCHER, JR. WILLIAM E. SCHUYLER, JR.
Attesting Officer Commissioner of Patents