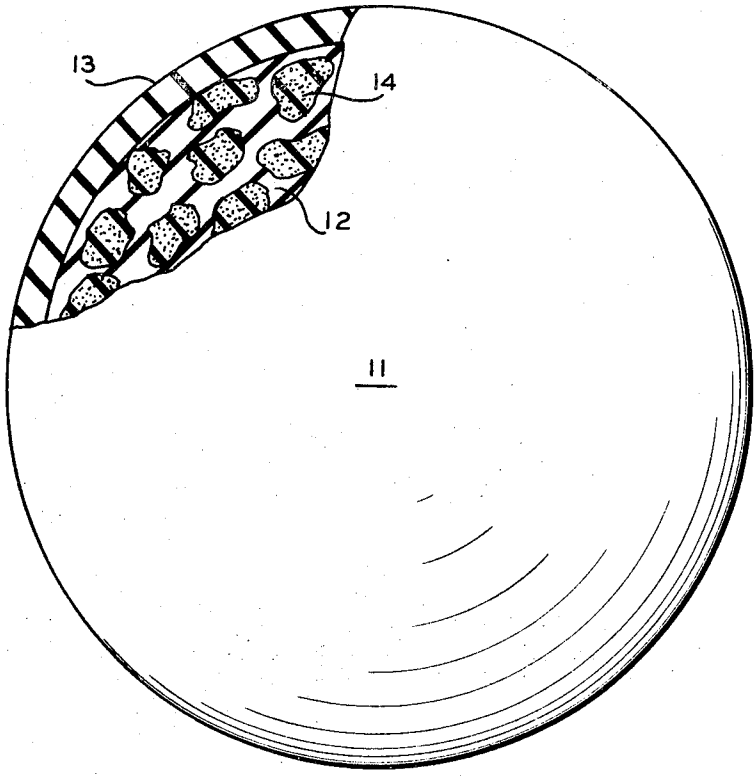
June 19, 1973 D. D. DEARMONT 3,740,354

BOWLING BALL CORE CONTAINING SPONGE RUBBER CHIPS

Filed Jan. 25, 1971




INVENTOR.
D. D. DEARMONT
BY
Young & Quigg
ATTORNEYS

United States Patent Office 3,740,354 Patented June 19, 1973



3,740,354

# BOWLING BALL CORE CONTAINING SPONGE RUBBER CHIPS

Donald D. Dearmont, Stow, Ohio, assignor to Phillips Petroleum Company

Filed Jan. 25, 1971, Ser. No. 109,179
Int. Cl. C08d 9/02, 13/08; A63b 37/06
U.S. Cl. 260—2.5 H 7 Claims

## ABSTRACT OF THE DISCLOSURE

A bowling ball comprising an exterior shell having a smooth outer rolling surface and an inner core, wherein said core comprises a binder or matrix material comprising a vulcanized natural or synthetic rubber having dispersed therein a multiplicity of discrete chips of natural or synthetic sponge rubber. Bowling balls containing the cores of the invention are characterized by improved dimensional stability and impact resistance.

This invention relates to bowling balls having a smooth outer rolling surface superimposed over a resilient core and to the method of manufacturing balls of its kind. More particularly, this invention relates to bowling balls having a new and improved core material comprising a vulcanized natural or synthetic rubber binder or matrix material having dispersed therein a multiplicity of discrete chips of natural or synthetic sponge rubber.

Typically, bowling ball manufacturers provide balls of a variety of weights, e.g., for use by men and women, the diameters and weights of which are governed by accepted regulations. In the manufacture of heavier weight bowling balls, higher density, structurally sound, impact-resistant materials are readily available and may be conventionally used. However, where it is desired to provide lighter weight bowling balls, a definite problem exists in obtaining economical, light weight materials with sufficient inherent structural properties and inherent impact-resistant properties to serve as bowling ball materials and especially as materials of construction of bowling balls. Typically, notwithstanding attempts to make bowling balls using a variety of materials such as urethane foams have met only minor acceptance. Light weight rubber balls or light weight bowling balls continue to use cork, wood chips, and sawdust as a material of construction in the manufacture of light weight bowling balls.

It has now been discovered that the use of low density, high hardness sponge rubber in combination with a vulcanizable binder material can be used to provide stock materials suitable for cores for bowling balls and similar shaped objects, which cores have improved structural properties, such as improved dimensional stability and improved impact resistance.

According to the invention, bowling balls, particularly light weight, i.e., 7 to 12 pounds, bowling balls comprising an exterior shell having a smooth outer rolling surface and an inner core comprising a vulcanized natural or synthetic rubber binder or matrix material having dispersed therein a multiplicity of discrete chips of natural or synthetic sponge rubber.

The accompanying drawing is a partial sectional view of a preferred bowling ball embodying the present invention. According to this drawing, there is provided a bowling ball **11** having a veneer or outer surface **13** superimposed upon a core material comprising a vulcanized synthetic or natural rubber **12** having dispersed therein a multiplicity of discrete chips **14** of natural or synthetic sponge rubber.

As a general rule, the veneer or exterior shell of bowling balls made according to the invention will be a natural rubber such as cis-1,4-polyisoprene or a synthetic rubber such as butadiene-styrene; neoprene; butyl rubber; nitrile rubber; polysulfide rubber; chlorosulfonated polyethylene; polyurethane; cis-1,4-polybutadiene; synethic cis-1,4-polyisoprene; adduct rubber; and combinations thereof. Curing of these materials is effected at elevated temperatures by suitable chemical agents well known in the art.



The inner core of the bowling balls made in accordance with the invention is composed of a cured, i.e., vulcanized, binder or matrix in which there are dispersed discrete chips of microcellular sponge rubber materials characterized by having a low density in combination with a high hardness.

Materials suitable for use as a matrix or binder in forming the cores of this invention are generally selected from the same group of materials generally used in forming the veneer or exterior shell. Thus, the binder consists of at least one material selected from the class consisting of natural rubber such as cis-1,4-polyisoprene; synthetic rubber such as butadiene-styrene, neoprene, butyl rubber, nitrile rubber, polysulfide rubber, chlorosulfonated polyethylene, cis-1,4-polybutadiene, synthetic cis-1,4-polyisoprene, adduct rubber and mixtures thereof. Preferred as matrix materials are the synthetic rubbers selected fom the group consisting of emulsion-polymerized and solution-polymerized elastomers of conjugated dienes containing 4 to 12, preferably 4 to 8, carbon atoms per molecule, including homopolymers and copolymers thereof; and including copolymers of such conjugated dienes with one or more copolymerizable monovinylidene monomers. Representative of such monomers which can be used in the preparation of the preferred matrix materials of the invention are

1,3-butadiene;
isoprene;
piperylene;
2,3-dimethyl-1,3-butadiene;
1,3-octadiene;
4,5-diethyl-1,3-octadiene;
styrene;
2-methylstyrene;
vinylnaphthalene;

and the like. The matrix elastomers, including the preferred solution- and emulsion-polymerized elastomers, can be prepared by any of the known processes for preparing elastomeric materials.

The sponge rubbers, suitable for use in forming the cores of this invention are selected from the same group of materials generally used as binder or matrix materials. Thus, the sponge rubbers comprise at least one material selected from the class consisting of natural rubbers such as cis-1,4-polyisoprene or synthetic rubbers such as butadiene-styrene, neoprene, butyl rubber, nitrile rubber, polysulfide rubber, chlorosulfonated polyethylene, cis-1,4-polybutadiene, synthetic cis-1,4-polyisoprene, and adduct rubber. Such sponge rubbers are prepared by various means known to the art. The sponge is comminuted as by grinding to form a crumb for admixture with the selected vulcanizable binder material(s).

The sponge rubbers which are preferred for use in the practice of the invention can be broadly defined as solution-polymerized elastomers obtained by the polymerization, in the presence of a suitable diluent which is a solvent for the polymer product and an alkali metal-based polymerization initiator including (1) an Alfin catalyst, (2) an organolithium compound or (3) an alkali metal, of conjugated dienes containing from 4 to 12, preferably

4 to 8, carbon atoms per molecule. Examples of monomers which can be used in the preparation of the polymers include

1,3-butadiene;
isoprene;
piperylene;
2,3-dimethyl-1,3-butadiene;
1,3-octadiene;
4,5-diethyl-1,3-octadiene;

and the like. These conjugated dienes can be polymerized to form homopolymers or mixtures of the dienes can be polymerized to form copolymers. Conjugated diene polymers can also be prepared by polymerizing the dienes with one or more copolymerizable monovinylidene monomers, such as styrene, 2-methylstyrene, vinylnaphthalene, and the like. Such polymers and copolymers can be prepared by known methods using any of the mentioned catalyst systems. Representative of such processes are those disclosed in U.S. Pats. 2,975,160 and 3,324,089, which disclose solution polymerization processes using organolithium catalysts; U.S. Pat. 3,285,901, which discloses solution polymerization processes using alkali metal catalyst systems; and U.S. Pat. 3,067,187, which discloses solution polymerization processes using Alfin catalysts. The solution polymers obtained from organolithium compound catalystic processes are preferred with 1,3-butadiene/styrene copolymers prepared according to the procedures of U.S. Pat. 3,234,089 being especially preferred.

A critical feature of the invention is the use in forming the cores of the invention of microcellular sponge rubber materials having a low density and a high hardness. Thus, sponge rubber materials having a density in the range of 0.33 to 0.49 and a Shore A hardness in the range of 40 to 55 after initial vulcanization can be used in forming the cores of the invention, with densities in the range of 0.38–0.44 and a Shore A hardness in the range of 45–50 being particularly preferred. As noted, any of the known natural and synthetic sponge rubbers, regardless of the method of preparation of such rubbers, can be used in preparing the cores of this invention, it only being necessary that they correspond to the delineated density and hardness ranges and that the rubber be in the shape of microcellular chips.

In preparing bowling balls according to the practice of the invention, any of the conventional processes now employed in the art can be used. Generally, the core material is compounded by homogeneously blending the microcellular sponge rubber chips with the vulcanizable natural or synthetic rubber matrix material, the recipe for which includes an appropriate vulcanization promoter.

Generally, the cores prepared according to the invention comprise by total weight 20 to 80 percent binder material and 80 to 20 percent sponge rubber, with compositions comprising 45 to 55 weight percent binder material and 55 to 45 weight percent sponge rubber being preferred. Especially preferred are compositions comprising equal weight amounts of sponge rubber and binder. It will be appreciated by those skilled in the art that the weight of bowling balls produced according to the invention can be controlled by varying the amounts of binder material and/or sponge rubber, varying the density of the sponge rubber, and by inclusion of filler material such as barium sulfate, particularly when heavier weight balls are desired.

The core material can be shaped into appropriate form, prevulcanized, and ground to the desired size, after which the surface or rolling layer can be superimposed over the core. In order that the invention may be more fully understood, the following illustrative example is provided. It will be understood that the invention is not to be limited to specific details enumerated. Parts are parts by weight unless otherwise expressed.



## EXAMPLE

A microcellular sponge rubber having a density of 0.41 (g./cc.) and a Shore A hardness of 48 was prepared from the following ingredients with a curing cycle of 10 minutes at 315° F.:

| | Parts by weight |
|---|---|
| Solprene 303[1] | 86 |
| Philprene 1614 | 21 |
| Polymer SS260 | 20 |
| HiSil 215 | 20 |
| Suprex Clay | 90 |
| Picco 6100 | 12.5 |
| Circo Light Oil | 3 |
| Agerite Superlite | 1 |
| Stearic acid | 4 |
| Zinc oxide | 3 |
| Carbowax 4000 | 1 |
| Aktone | 2 |
| MBTS | 0.5 |
| Sulfur | 3 |
| Unicel ND | 4 |

The sponge rubber was ground to a fine crumb and formulated into a bowling ball core, using as a binder material equal weight amounts of, in one instance, a Solprene 1205[1] synthetic rubber and, in a second instance, a SBR 3110 synthetic rubber. For comparison purposes, ground cork in an amount equal to that of the sponge rubber was combined with equal weight amounts of the same binder materials. The impact resistance of the respective cores is reported in the following table:

IMPACT RESISTANCE (INCH-POUNDS) OF GROUND MICROCELLULAR SPONGE VS. GROUND CORK

| Binder | Ground cork filler | Solprene 303[1] filler |
|---|---|---|
| Solprene 1205[1] | 30 | 45 |
| SBR 3110 | 30 | 42 |

[1] Phillips trademark.

The example demonstrates that the combination of microcellular sponge rubber chips in combination with a vulcanizable matrix provides stock material having materially improved impact resistance.

Listed below are the identification of various ingredients and test methods employed in the foregoing example:

(1) Solprene 303[1]—Solution-polymerized butadiene/styrene (52/48) block copolymer having a Mooney viscosity of 40–50 and a density of 0.920 g./cc. (Phillips Petroleum);
(2) Philprene 1614—Cold rubber black masterbatch; 23.5% bound styrene (Phillips Petroleum);
(3) Polymer SS260—SBR-type polymer blended with a high styrene resin (75% styrene) (Polymer Corp.);
(4) HiSil 215—Precipitated hydrated silica (PPG Industries);
(5) Suprex Clay—Hydrated aluminum silicate (J. M. Huber);
(6) Picco 6100—Aromatic polyindene resin (Pennsylvania Industrial Chemicals);
(7) Circo Light Oil—Naphthenic oil (Sun Oil);
(8) Agerite Superlite—Polybutyl Bisphenol A mixture, an antioxidant (R. T. Vanderbilt);
(9) Carbowax 4000—Polyethylene glycol (Union Carbide);
(10) Aktone—Urea complex, activator (J. M. Huber);
(11) MBTS—2,2'-benzothiazyl disulfide, accelerator (American Cyanamid);
(12) Unicel ND—N,N'-dinitrosopentamethylene tetramine, blowing agent (E. I. du Pont);

[1] Phillips trademark.

(13) Solprene 1205 [1]—Solution-polymerized butadiene/styrene (75/25) block copolymer having a Mooney viscosity of 42–52 and a density of 0.930 g./cc.;
(14) SBR 3110—Emulsion-polymerized butadiene/styrene;
(15) Mooney Viscosity, ML–4 at 212° F.—ASTM D 1646–63;
(16) Shore A Hardness—ASTM D 1706–61; and
(17) Method for determining impact resistance—by falling weight test (ASTM D 639–60T modified).

While certain embodiments of the invention have been described for illustrative purposes, the invention is not limited thereto. Various other modifications or embodiments of the invention will be apparent to those skilled in the art in view of this disclosure. Such modifications or embodiments are within the spirit and scope of the disclosure.

[1] Phillips trademark.

I claim:

1. A bowling ball core consisting essentially of a vulcanized elastomer matrix, wherein said matrix is selected from the group consisting of emulsion-polymerized polymers of diolefins having from 4 to 12 carbon atoms and copolymers of diolefins having from 4 to 12 carbon atoms and one or more copolymerizable monovinylidene monomers containing 8 to 10 carbon atoms or solution-polymerized elastomers obtained by the polymerization, in the presence of a solvent for an elastomer product and an alkali metal-based polymerization initiator selected from the group consisting of (1) an Alfin catalyst, (2) an organolithium compound or (3) an alkali metal, of at least one conjugated diene having 4 to 12 carbon atoms or copolymers of such dienes and copolymerizable monovinylidene monomers, containing dispersed therein a multiplicity of macroscopic chips of at least one sponge rubber, said sponge rubber having a density in the range of 0.33 to 0.49 and a Shore A hardness in the range of 40 to 55 after initial vulcanization, wherein said sponge rubber is selected from the group consisting of solution-polymerized elastomers obtained by the polymerization, in the presence of a solvent for the elastomer product and an alkali metal-based polymerization initiator selected from the group consisting of (1) an Alfin catalyst, (2) an organolithium compound, or (3) an alkali metal, of at least one conjugated diene containing from 4 to 12 carbon atoms or copolymers of such dienes and one or more copolymerizable monovinylidene monomers, and wherein the amount of said matrix is in the range of 20 to 80 weight percent, based on the weight of the core, and the amount of said sponge rubber is in the range of 80 to 20 weight percent, based on the weight of the core.

2. A bowling ball core according to claim 1 wherein said sponge rubber is poly(butadiene-styrene).

3. A bowling ball core according to claim 1 wherein said matrix is selected from the group consisting of solution-polymerized elastomers obtained by the polymerization, in the presence of a solvent for the polymer product and an alkali metal-based polymerization initiator selected from the class consisting of (1) an Alfin catalyst, (2) an organolithium compound or (3) an alkali metal, of at least one conjugated diene containing from 4 to 12 carbon atoms or copolymers of such dienes and one or more copolymerizable monovinylidene monomers.

4. A bowling ball core according to claim 1 wherein said matrix is selected from the group consisting of emulsion-polymerized elastomers of at least one conjugated diene containing from 4 to 12 carbon atoms and copolymers of such dienes with one or more copolymerizable monovinylidene monomers.

5. A bowling ball core according to claim 2 wherein said poly(butadiene-styrene) is prepared by the solution polymerization of 1,3-butadiene and styrene in the presence of an organolithium initiator.

6. A bowling ball core according to claim 5 wherein said matrix is emulsion-polymerized poly(butadiene-styrene).

7. A bowling ball core according to claim 5 wherein said matrix is solution-polymerized poly(butadiene-styrene).

**References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,870,489 | 1/1959 | Rockoff | 260—2.5 H |
| 2,925,396 | 2/1960 | Pearson et al. | 260—2.3 |
| 3,206,201 | 9/1965 | Hendricks | 260—2.5 B |


JOHN C. BLEUTGE, Primary Examiner

W. J. BRIGGS, Sr., Assistant Examiner

U.S. Cl. X.R.

260—2.5 B, 2.5 HB, 5, 894; 273—58 J, 63 R