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HIGHLY RESILIENT POLYBUTADIENE BALL

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This is a continuation-in-part of application Serial No. 462,081 filed June 7, 1965, and now abandoned.

This invention relates to a toy and more particularly to a ball or sphere having extremely high resilience and a high coefficient of friction.

The resilience of rubber balls is one of their most important characteristics. This is because the resilience of the ball material determines the "liveliness" and "bounce" of the ball and hence its utility in various sporting games and attractiveness as a toy for children. The resilient material normally used for making rubber balls is a polymer such as natural rubber or some synthetic analog of natural rubber such as polyisoprene.

The present invention is concerned with a material other than rubber and polyisoprene as the base polymer in rubber toys and sporting articles.

It has been found that this new material imparts some highly unusual qualities to articles fabricated with it. Such articles have been found to have a substantially greater resiliency than those manufactured from more conventional materials. The greater resiliency is thought to be due to the nature of the base polymer used in the mixture and the unique quality of the mixture which comprises the article of being able to conserve the energy which is imparted to it rather than dissipating a substantial portion of it in the form of heat.

The higher resilience means that balls made from the material of this invention have a resilience factor in excess of 90%. This resilience

factor is the resilience of the material as measured by the Yerzley method, ASTM D945-59.

Another unusual quality of balls and toys of this invention is their coefficient of friction. In this instance the coefficient friction is substantially higher than in other similar items. This quality combined with the significantly higher resilience causes a ball to react in an extraordinary and unpredictable manner when bounced or struck. This higher coefficient of friction also provides a means whereby the spin or "English" on a thrown, struck or dropped ball can be accentuated resulting in unusual reactions by the ball whenever rebounds from a hard surface. This novel combination of qualities means that one natural application for balls manufactured with the base polymer with which this invention is concerned is in trick ball uses. In addition, as a sports implement a ball of this invention presents a greater challenge to the user. As an article of play, the eccentricity of reaction makes the ball a highly entertaining and amusing toy.

The invention in the present case contemplates a molded, vulcanized, highly resilient ball comprising a mixture of Polybutadiene, a sulfurous vulcanizing agent and a Polybutadiene reinforcing agent.

In addition to the inherent resilience of the base polymer, the degree of cross linkage between polymer chains is important in optimizing the bounce or liveliness of balls fabricated with it. The degree of cross linkage is primarily determined by the amount of vulcanizing agent used. By limiting the amount of vulcanizing agent introduced into the mixture to the quantities specified below, a ball having a Yerzley resilience in excess of 90% is obtained. Such a resilience factor is substantially higher that that found in balls manufactured from natural rubber or polyisoprene.

In addition to resilience and cross linkage, the ability of the material to conserve energy is of

importance. It has been found that balls manufactured according to the present invention dissipate very little energy imparted to it in the form of heat. The present invention embodies these and other properties as will be observed from the following detailed description.

In addition to the ingredients just previously discussed, 4 methyl-6 tertiary-butyl phenol is also added to the mixture. This substance has been given the trade name of Antioxidant 2246 and prevents discoloration and staining and inhibits aging of the finished product. Examples of substitutes for Antioxidant 2246 are phenyl B naphthylamine, alkyl diphenylamine, and hindered alkyl phenols. Pigmenting agents for obtaining the desired color of the end product are optional additives. The mixture and molding of the constituents of this formulation proceeds according to the following steps. The various elements of the formulation are brought together in a mixing machine and agitated thoroughly to insure uniform mixing and distribution of the elements throughout the mixture. The result is a plastic mass ready for insertion in a mold.

To complete the process, the mixture is placed in a mold and subjected to a pressure of between 500 and 3,000 p.s.i. for a period of approximately 10-30 minutes. Simultaneously, the temperature of the mixture is raised to approximately 285-340° F. To a certain extent the length of the molding operation, the pressure, and the temperature to which the formulation is subjected are co-variant and one may be adjusted to compensate for a variation of the other. Preferably the time and temperature for the molding operation is 15-20 minutes at approximately 320° F. and 1,000 p.s.i.

An alternate formulation to the one outlined above is as follows:

Constituent	Preferred, parts by wgt.	Range, parts by wgt.
Polybutadiene	100.00	
Zinc oxide	4.0	3-5
Stearic acid	2.0	0.5-3
Akron 544 Red	.25	0-1.0
Akron 626 Blue	.25	0-1.0
Titanium dioxide	.25	0-1.0
Zeolex	7.5	5-15
Vandex	.10	0-1.0
N-oxydiethylene benzothiazole 2 sulfenamide (AMAX)	1.75	0.5-2.5
Tetramethylithiuram disulfide (M. Tuads)	7.5	5-15
Sulfur	5.25	0.5-15

The above formulation is mixed in the same manner as the preceding formulation. To insure a good dispersion of all ingredients in the mixture, the batch is normally given a two-pass mix. In the above formulation, the zinc oxide and the stearic acid perform the same functions, viz., activation of polymer curing, as they did in the first formulation. Akron 544 Red and Akron 626 Blue are trade designations for organic coloring agents manufactured by Akron Chemical Co. Titanium dioxide is also a coloring agent. These three constituents in combination are the pigmenting agent for the mixture.

Zeolex is a proprietary brand name for a series of precipitated, highly hydrated sodium silico-aluminates and sodium calcium silico-aluminates. Its function is to strengthen the finished product and to act as a filler in the same manner as the Hi-Sil 233 does in the preceding formulation.

Sulfur is the vulcanizing agent. Vandex is a proprietary name for finely ground selenium. Its function is to supplement sulfur as a vulcanizing agent.

As in the first formulation, several constituents of the mixture (AMAX and M. Tuads) are added to serve as accelerators for the polymerization.

The accompanying diagrammatic drawing with legends illustrates the ball.

Products according to this invention are manufactured from a formulation consisting of the following:

Constituent	Preferred, parts by wgt.	Range, parts by wgt.
Polybutadiene	100.00	3-5
Zinc oxide	4.0	
Stearic acid	2.0	0.5-3
N-oxydiethylene benzothiazole 2 sulfenamide (AMAX)	1.75	0.5-2.5
Di-ortho-tolylguanidine (DOTG)	1.00	0.5-2.5
Bismuth dimethyldithio-carbonate (Bismate)	0.35	0.25-0.75
4 methyl-6 tertiary-butyl phenol	1.00	0.5-2
Hydrated silica	7.5	5-15
Sulfur	5.25	0.5-15

In the formulation above Polybutadiene is the base polymer of the mixture. To produce cross linkage between polybutadiene chains, that is, to vulcanize or cure the polymer, sulfur is added to the mixture. A greater amount of vulcanizing agent is used in the mixture than in such products as tires thereby producing a greater degree of vulcanization. Put another way, the degree of cross linkage relative to saturation (hard rubber) is increased over tires and the like.

The more complete vulcanization is believed to result in the improved resilience of the finished product. The addition of sulfur in the range indicated will result in balls having a Yerzley Resilience in excess of 90%. Oil extended polybutadiene having as much as 50 parts by weight of oil per hundred parts by weight of polybutadiene can also be used as the base polymer.

Because the natural curing rate of a mixture of polybutadiene and sulfur is quite slow, certain other additives are combined with this basic mixture to initiate the curing cycle and accelerate the rate of vulcanization. The zinc oxide and stearic acid are added to the basic mixture to provide this activation function. Acceleration accomplishes two purposes, one, it shortens the length of the molding cycle, and two, it equalizes heat throughout the mixture during the curing cycle. In the preceding formulation, the accelerators are N-oxydiethylene benzothiazole 2 sulfenamide, di-orthotolylguanidine and bismuth dimethyldithiocarbonate. For ease of reference, the trade names AMAX, DOTG and Bismate respectively will be used to designate the accelerators.

This activation of these accelerators occurs as the mixture reaches a specific temperature. For Bismate and DOTG the activation temperature is approximately 230° F, while that of AMAX is approximately 260° F. By insuring that the heat of reaction is equalized throughout the mixture a more uniform rate of vulcanization and improved consistency in the end product is obtained.

Hydrated silica is added to the mixture as a filler. As specific hydrated silica suitable for use in this mixture is marked under the trademark Hi-Sil 233. This material and certain other materials perform the function of providing tear and abrasion resistance. The basic criteria for selection of the filler material is its ability to improve the durability of polybutadiene with unduly increasing the specific gravity. Carbon black and lithium oxide have also been found to fill these requirements and are satisfactory substitutes for hydrated silica.

As is normal in molding techniques, the curing temperature must be carefully selected in order to prevent imperfections in the finished product. Too high a molding temperature will contribute to a condition designated "backrind." This condition is characterized by an indented fracture around the body of the molded product defining the point where the two halves of the mold are brought together and is due to thermal expansion in this area during and after the molding cycle.

Subject to the proper choice of injection pressure, injection time, and the combination of mixture constituents, preheat, and mold temperature, this mixture can also be molded by means of a conventional injection-molding technique.

Combinations of ingredients of which the two formulations listed above are representative have been found to result in a product with a specific gravity of approximately 1.0 to 1.3. For greatest resilience, it has been found that a sufficient amount of filler should be added to produce a product having a specific gravity of 1.02.

What is claimed is:

1. A highly resilient solid ball in the form of a sphere, the ball material having a specific gravity of from about 1 to about 1.3, and comprising in combination a vulcanized polymer characterized by the use of 100 parts by weight of polybutadiene and 0.5 to 15 parts by weight of a sulfur vulcanizing agent, and further comprising, in addition to any activators and accelerators used for vulcanization, 5 to 15 parts by weight of an inorganic reinforcement material.

2. A ball is in accordance with claim **1** in which the reinforcing material is selected from the class consisting of hydrated silica, carbon black and lithium oxide.

3. A ball in accordance with claim **2** in which the sulfur vulcanizing agent is approximately 5.25 parts by weight and the reinforcing material is approximately 7.5 parts by weight.

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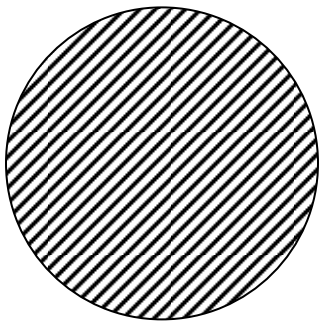

BALL MATERIAL:

SPECIFIC GRAVITY	- 1-1.3
POLYBUTADIENE	- ABOUT 100 PARTS
SULFUR VULCAN. AGENT	- 0.5 to 15 PARTS
HYDRATED SILICA or } CARBON BLACK or } LITHIUM OXIDE }	- 5 to 15 PARTS

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