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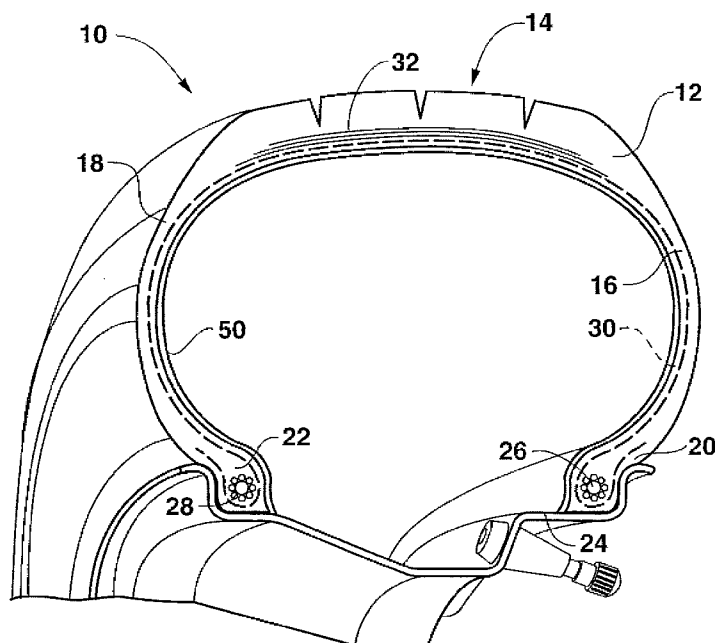
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(54) **Title:** RUBBER COMPOSITION FOR BARRIER LAYER



**FIG. 1**

(57) **Abstract:** An article such as a pneumatic tire having a barrier layer that minimizes the leakage of inflation gases through the tire. The barrier layer includes an elastomer as well as between 1 and 50 phr of glass microspheres, ceramic microspheres or combinations thereof. Surprisingly, the addition of the microspheres provides a significant decrease in the gas permeability of the tire. The microspheres may be solid or hollow. The elastomer may include many types of elastomer compounds and is limited only by the particular application. Because of the significant decrease in the gas permeability through the barrier layer having microspheres, a wider selection of elastomer compositions may be available for use in the barrier layer, i.e., those elastomers that were not previously typically selected for use in a barrier layer because of their unacceptably high gas permeability property may now be used because of the highly effective blocking by the microspheres.

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## RUBBER COMPOSITION FOR BARRIER LAYER

### BACKGROUND OF THE INVENTION

#### Field of the Invention

[0001] This invention relates generally to gas-inflated articles and more specifically, to barrier layers within the inflated articles that decrease the diffusion of the gas from the article.

#### Description of the Related Art

[0002] Various articles are constructed to hold gas, such as air, under pressure. These articles include, for example, tires, athletic balls such as basketballs, footballs and tennis balls, inflatable boats, air mattresses, and the like. These articles are typically made from a polymeric material having some elastic properties. Tires, for instance, are typically made from an elastomeric rubber material, such as a styrene butadiene polymer.

[0003] Many elastomeric materials used to make inflatable articles may, in some circumstances, remain slightly permeable to gases. If left unchecked, the gas permeability of the inflated article may compromise the performance of the article and cause the article to deflate over time. Furthermore, if the gas that passes through the slightly permeable material is oxygen, then the oxygen can cause oxidation of the elastomers, causing deleterious effects to the properties of the elastomer, *e.g.*, the elastomers may tend to harden and degrade.

[0004] In view of the above, it is often advantageous for inflatable articles to contain a barrier layer that reduces gas permeability and inhibits oxygen travel through the article. Often, in the past, these barrier layers have been made from a composition containing butyl rubber. Butyl rubber in its raw state, however, still remains somewhat gas permeable. Thus, many attempts have been made to combine butyl rubber with other materials in order to further reduce permeability.

### SUMMARY OF THE INVENTION

[0005] Particular embodiments of the present invention include a pneumatic tire having a barrier layer that minimizes the leakage of inflation gases through the tire. The

barrier layer includes an elastomer as well as between 1 and 50 phr of glass microspheres, ceramic microspheres or combinations thereof. Surprisingly, the addition of the microspheres provides a significant decrease in the gas permeability of the tire.

[0006] The microspheres may be solid or hollow. However, if the spheres are hollow, the spheres should have a crush strength of at least 2,000 psi. The elastomer may include many types of elastomer compounds and is limited only by the particular application. Because of the significant decrease in the gas permeability of the barrier layer having microspheres, a wider selection of elastomer compositions may be available for use in the barrier layer, *i.e.*, those elastomers that were not previously typically selected for use in a barrier layer because of their unacceptably high gas permeability property may now be used because of the highly effective blocking by the microspheres.

[0007] Particular embodiments of the present invention may further include a terpene resin having a glass transition temperature greater than about 50°C and a softening point of less than about 170°C. Additionally, particular embodiments may contain permeability reducing mineral fillers.

[0008] Particular embodiments may also include an article having a barrier layer as described above, wherein the article may be, for example, an inflatable sports ball

[0009] The foregoing and other objects, features and advantages of the invention will be apparent from the following more descriptions of particular embodiments of the invention, as illustrated in the accompanying drawing wherein like reference numbers represent like parts of the invention.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0010] FIG. 1 is a cross sectional view of one embodiment of a tire incorporating a barrier layer made according to the present invention.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0011] Particular embodiments of the present invention include barrier layers and elastomeric inflatable articles that hold a pressurized gas as an inflating gas, *e.g.*, air, nitrogen, inert gases and the like. Barrier layers that are included as particular embodiments of the

present invention may be incorporated into, for example, tires, sports equipment, such as sport balls, and in other articles in which an internal air pressure must be maintained.

[0012] When incorporated into the wall of an elastomeric article, a barrier layer reduces the gas, vapor, and/or chemical permeability of the article. When incorporated into an inflatable article, a barrier layer not only improves the performance of the article by inhibiting gases from leaking out of the article, but also serves to protect the article from, for example, oxidation due to oxygen migration. In the description of the invention and examples disclosed herein, a reference to improvements or reduction in permeability means a lowering of the leak rate of gas, vapor, and/or chemicals from the article.

[0013] The composition that is used to form the barrier layer of particular embodiments of the present invention generally includes an elastomer or a blend of elastomers combined with microspheres. Microspheres are readily available in either a solid or hollow form in a wide variety of diameters. Particular embodiments of the invention include glass microspheres, ceramic microspheres or combinations thereof.

[0014] Particular embodiments of the present invention include glass microspheres, such as, for example, those made of soda-lime-borosilicate glass. Glass microspheres, including those made of soda-lime-borosilicate glass, are available, for example, from 3M Specialty Materials located in Minnesota under the trade name SCOTCHLITE. Particular embodiments of the invention include ceramic microspheres, such as, for example, those made of silica-alumina ceramics and are available both as a hollow product or a solid product. Ceramic microspheres, including those made of silica-alumina ceramics, are available, for example, from 3M under the trade name Z-Light microspheres, which are hollow. It should be noted that embodiments of the present invention include the use of hollow and solid microspheres, or combinations thereof. Both hollow and solid microspheres are available, for example, from 3M.

[0015] The microspheres may be coated with a coupling reagent to bond with the elastomer matrix. For example, the glass microspheres may be silane treated with a silane coupling reagent such as, for example, bis-[3-(triethoxysilyl)-propyl]-tetrasulfide (TESPT). The ceramic microspheres may be coated with an epoxy silane surface treatment such as, for example, as available from 3M as SCOTCHLITE Floated Product Series, H20/1000 and

H50/10,000 EPX. The invention is not meant to be limited by these examples of coated microspheres as other useful coatings may also be applied to the microspheres as known to those having ordinary skill in the art and as may be desirable for given applications.

[0016] The diameters of the microspheres useful for the present invention may vary. For example, without limiting the invention, particular embodiments include glass microspheres having a diameter of the 50<sup>th</sup> % distribution (by volume) of between 40 and 70 microns with a diameter of the 90<sup>th</sup> % distribution (by volume) of between 40 and 115 microns. The ceramic microspheres may have a diameter of the 50<sup>th</sup> % distribution (by volume) of between 40 and 130 microns with a diameter of the 90<sup>th</sup> % distribution (by volume) of between 100 and 300 microns. It should be noted that these diameters are not meant to limit the invention and any useful diameter or distribution of diameters are within the scope of embodiments of the present invention.

[0017] The microspheres are surprisingly successful in reducing the leakage of inflation gases through the barrier layer of an inflated article. Results from laboratory studies of the embodiments of the present invention have shown improvements of 37 to 46% permeability improvements with only very minor impacts on other physical properties.

[0018] Particular embodiments of the present invention may further comprise, in addition to microspheres, a terpene resin having a relatively high glass transition temperature. The glass microspheres dispersed within the elastomer are present in order to reduce the gas permeability characteristics of the material. The terpene hydrocarbon resin having a relatively high glass transition temperature is present for various reasons that include, for example, without limiting the invention, improving the dispersability of the permeability reducing particles, improving the processability of the composition by lowering the modulus and the viscosity of the composition and further reducing the gas permeability of the material.

[0019] The terpene resin useful for embodiments of the present invention may be unmodified and may include, for example, polylimonene, polyalphapinene, polybetapinene, or mixtures thereof. "Terpene resins" as used herein are known to those having ordinary skill in the art to be terpene resins that are polyterpene resins based upon alpha and beta pinene or combinations thereof and do not include in particular tall oil derivatives, rosin derivatives, terpene phenolic resins and hydroxylated polyesters.

[0020] The terpene resin may have a relatively low molecular weight, such as less than about 2000. As described above, terpene hydrocarbon resins for use in particular embodiments of the present invention generally have a relatively high glass transition temperature. For instance, the glass transition temperature of the terpene hydrocarbon resin is greater than about 50°C, and may be greater than about 60°C, or even greater than about 70°C. The terpene resin should further have a softening point that is compatible with the processing of the other materials contained in the composition. For example, when forming a barrier layer, the terpene resin is mixed, heated, and melted with the other components in the composition. Thus, the terpene resin should have a softening point that is less than the temperature at which other ingredients in the composition, such as the elastomer, begin to degrade and break down. When the elastomer combined with the terpene resin is a butyl rubber, for instance, it is advantageous for the terpene resin to have a softening point of less than about 170°C, such as less than about 140°C. In other applications, however, the softening point of the terpene resin may be higher than the above temperatures. As used herein, the softening point is determined by the “Ring and Ball” method such as described in ASTM E-28.

[0021] Commercially available terpene resins that may be used in the present invention include a polyalphapinene resin marketed under the name Resin R2495 by Hercules Inc. of Wilmington, DE. Resin R2495 has a molecular weight of about 932, a softening point of about 135°C and a glass transition temperature of about 91°C. Another commercially available product that may be used in the present invention includes DERCOLYTE L120 polylimonene resin sold by the company DRT of France. DERCOLYTE L120 polylimonene resin has a molecular weight of about 877, has a softening point of about 119°C, and has a glass transition temperature of about 73°C. Still another commercially available terpene resin that may be used in the present invention includes SYLVARES 7125 polylimonene resin sold by the Arizona Chemical Company of Jacksonville, FL. SYLVARES 7125 polylimonene resin has a molecular weight of about 102, has a softening point of about 125°C, and has a glass transition temperature of about 73°C.

[0022] The amount of terpene resin present in the composition depends upon the particular circumstances and the desired result. In general, for instance, the terpene resin may

be present in the composition in an amount from about 1 to about 50 phr, such as from about 1 to about 35 phr. For instance, in one embodiment, the resin may be present in the composition in an amount from about 5 phr to about 20 phr.

[0023] Particular embodiments of the present invention may further comprise, in addition to microspheres and/or the terpene resin, generally any permeability reducing mineral fillers. Such permeability reducing mineral fillers are capable of reducing the gas permeability characteristics of a film or layer formed from the composition, thanks to its form, size or shape factor, generally known as "platy filler" (*i.e.*, under the form of plates, platelets, layers, stacked layers or platelets, etc). Examples of fillers that may be used in order to reduce the gas permeability of the barrier layer include silicates, such as phyllosilicates. Such materials include, for instance, smectite clay minerals and various other clay materials. Particular examples include kaolin, montmorillonite such as sodium montmorillonite, magnesium montmorillonite, and calcium montmorillonite, nontronite, beidellite, volkonskoite, hectorite, laponite, sauconite, sobockite, stevensite, svinfordite, vermiculite, mica, bentonite, sepeolite, saponite, and the like. Other materials that may be used include micaceous minerals such as illite and mixed layered illite/smectite minerals, such as ledikite and admixtures of illites and the clay minerals described above. Other suitable materials include graphite and/or glass flake, either alone or mixed with other permeability reducing mineral fillers.

[0024] In particular embodiments, an organo-modified filler may be used. For instance, an organo-modified phyllosilicate may be incorporated into the composition of the present invention. In one particular embodiment, the organic structure to which the filler is associated is a surfactant. The surfactant, for instance, may be represented by the following formula:



wherein M denotes nitrogen, sulfur, phosphorous or pyridinium, and R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> independently denote hydrogen atoms, alkyl groups, aryl groups, or allyl groups, which may be the same or different.

[0025] In particular embodiments of the present invention, for example, an organic modified montmorillonite based clay may be used. The montmorillonite clay may be



organically modified with a surfactant, for instance, dimethyl-dihydrogenated tallow-quaternary ammonium salt. An organically modified montmorillonite based clay as described above is commercially available from Southern Clay Products under the trade names CLOISITE 6A, 15A, and 20A. CLOISITE 6A, for instance, contains 140 meq/100 g clay of dimethyl dihydrogenated tallow quaternary ammonium salts. In addition to dimethyl-dihydrogenated tallow-quaternary ammonium salts, in other embodiments, the clay may also be organically modified with an octadecylamine or a methyl-tallow-bis-2-hydroxyethyl quaternary ammonium salt. Still other surfactants that may be used to modify the particles include dimethyl ditallow ammonium, dipolyoxyethylene alkyl methyl ammonium, trioctyl methyl ammonium, polyoxypropylene methyl diethyl ammonium, dimethyl benzyl hydrogenated tallow quaternary ammonium, dimethyl hydrogenated tallow 2-ethylhexyl quaternary ammonium, methyl dihydrogenated tallow ammonium, and the like. In addition to surfactant modification, the edges of montmorillonite clays may also be silane modified. For example, permeability reducing particles edge treated with silane agents are available under the trade name Nanomer I.31PS from Nanocor, Inc. of Arlington Heights, Illinois.

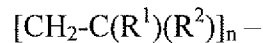
[0026] In addition to montmorillonite based clays, the permeability reducing mineral fillers may comprise a synthetic mica (synthetic or natural), vermiculite, and bentonite based clay. Synthetic micas are commercially available from Co-Op Chemical Co., Ltd. under the trade name SOMASIF. Bentonite based clays are commercially available from Elementis Specialties/Rheox, Inc. under the trade name BENTONE.

[0027] The amount of the permeability reducing mineral fillers present in the composition depends generally on the particular particles selected and the materials they are being mixed with. In general, the permeability reducing mineral fillers may be present in the composition in an amount from about 1 to about 25 phr, such as from about 5 to about 20 phr. In an alternative embodiment, the particles may be present in the composition in an amount from about 3 to about 15 phr.

[0028] Particular embodiments of the present invention, in addition to the microspheres and/or the resin and/or the permeability reducing mineral fillers, also include an elastomer. The elastomer may comprise any suitable rubber-like material that has the desired permeability characteristics. The elastomer may be, for instance, a natural rubber, a butyl

rubber, or a diene rubber such as, for example, an isoprene rubber. Particular embodiments of the rubber composition include blends of one or more of these elastomers.

[0029] In particular embodiments, for example, the elastomer may comprise a vinyl-based polymer. For example, the elastomer may be a polymer represented by the following general formula:



wherein  $\text{R}^1$  and  $\text{R}^2$  are independently hydrogen, an alkyl group, an aryl group, or an allyl group and wherein  $\text{R}^1$  and  $\text{R}^2$  may be the same or different.

[0030] The monomer used to form the above polymer may include, but is not limited to, ethylene, propylene, butadiene, isoprene, chloroprene, vinyl chloride, vinylidene chloride, vinyl fluoride, vinylidene fluoride, styrene, and alpha-methylstyrene.

[0031] In certain embodiments, the elastomer may have a polar functionality. For example, in one embodiment, the elastomer may be halogenated and may contain a halogen functional group such as bromine, chlorine, or fluorine.

[0032] Particular embodiments may include an elastomer that comprises epichlorohydrin polymers, which are available, for example, from Zeon Corporation under the trade name HYDRIN. These polymers are useful because, *inter alia*, they have a lower gas permeability as desired in barrier layers.

[0033] For particular embodiments, the elastomer comprises a diene rubber. "Diene" elastomer or rubber is understood to mean, in known manner, an elastomer resulting at least in part (*i.e.* a homopolymer or a copolymer) from diene monomers (monomers bearing two double carbon-carbon bonds, whether conjugated or not).

[0034] In general, "essentially unsaturated" diene elastomer is understood here to mean a diene elastomer resulting at least in part from conjugated diene monomers, having a content of members or units of diene origin (conjugated dienes) which is greater than 15% (mol %).

[0035] Thus, for example, diene elastomers such as butyl rubbers or copolymers of dienes and of alpha-olefins of the EPDM type do not fall within the preceding definition, and may in particular be described as "essentially saturated" diene elastomers (low or very low content of units of diene origin which is always less than 15%).

[0036] Within the category of "essentially unsaturated" diene elastomers, "highly unsaturated" diene elastomer is understood to mean in particular a diene elastomer having a content of units of diene origin (conjugated dienes) which is greater than 50%.

[0037] These definitions being given, the following are understood as non-limiting examples of diene elastomers that are useful in particular embodiments of the present invention:

[0038] - any homopolymer obtained by polymerization of a conjugated diene monomer having 4 to 12 carbon atoms;

[0039] - any copolymer obtained by copolymerization of one or more dienes conjugated together or with one or more vinyl aromatic compounds having 8 to 20 carbon atoms;

[0040] - a ternary copolymer obtained by copolymerization of ethylene, of an  $\alpha$ -olefin having 3 to 6 carbon atoms with a non-conjugated diene monomer having 6 to 12 carbon atoms, such as, for example, the elastomers obtained from ethylene, from propylene with a non-conjugated diene monomer of the aforementioned type, such as in particular 1,4-hexadiene, ethylidene norbornene or dicyclopentadiene;

[0041] - a copolymer of isobutene and isoprene (butyl rubber), and also the halogenated, in particular chlorinated or brominated, versions of this type of copolymer.

[0042] Suitable conjugated dienes are, in particular, 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-di(C1-C5 alkyl)-1,3-butadienes such as, for instance, 2,3-dimethyl-1,3-butadiene, 2,3-diethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-isopropyl-1,3-butadiene, an aryl-1,3-butadiene, 1,3-pentadiene and 2,4-hexadiene. Suitable vinyl aromatic compounds are, for example, styrene, ortho-, meta- and para-methylstyrene, the commercial mixture "vinyltoluene", para-tert.-butylstyrene, methoxystyrenes, chlorostyrenes, vinylmesitylene, divinylbenzene and vinylnaphthalene.

[0043] The copolymers may contain between 99% and 20% by weight of diene units and between 1% and 80% by weight of vinyl aromatic units. The elastomers may have any microstructure, which is a function of the polymerization conditions used, in particular of the presence or absence of a modifying and/or randomizing agent and the quantities of modifying and/or randomizing agent used. The elastomers may for example be block, statistical,

sequential or micro-sequential elastomers, and may be prepared in dispersion or in solution; they may be coupled and/or starred or alternatively functionalized with a coupling and/or starring or functionalizing agent.

[0044] Polybutadienes (BR) are suitable, and in particular those having a content of 1,2-units of between 4% and 80%, or those having a cis-1,4 content of more than 80%; polyisoprenes, butadiene-styrene copolymers, and in particular those having a styrene content of between 5% and 50% by weight and, more particularly, between 20% and 40%, a content of 1,2-bonds of the butadiene part of between 4% and 65%, and a content of trans-1,4 bonds of between 20% and 80%; butadiene-isoprene copolymers and in particular those having an isoprene content of between 5% and 90% by weight and a glass transition temperature ("Tg" measured according to ASTM D3418-82) of -40°C to -80°C; isoprene-styrene copolymers and in particular those having a styrene content of between 5% and 50% by weight and a Tg of between -25°C and -50°C.

[0045] In the case of butadiene-styrene-isoprene copolymers, those which are suitable are in particular those having a styrene content of between 5% and 50% by weight and, more particularly, between 10% and 40%; an isoprene content of between 15% and 60% by weight, and more particularly between 20% and 50%; a butadiene content of between 5% and 50% by weight, and more particularly between 20% and 40%; a content of 1,2-units of the butadiene part of between 4% and 85%, a content of trans-1,4 units of the butadiene part of between 6% and 80%, a content of 1,2- plus 3,4-units of the isoprene part of between 5% and 70%, and a content of trans-1,4 units of the isoprene part of between 10% and 50%; and more generally any butadiene-styrene-isoprene copolymer having a Tg of between -10°C and -70°C.

[0046] In summary, the diene elastomer may be selected from the group of highly unsaturated diene elastomers which comprises polybutadienes (BR), polyisoprenes (IR), natural rubber (NR), butadiene copolymers, isoprene copolymers, and mixtures of these elastomers.

[0047] Such copolymers are selected from the group which comprises styrene-butadiene copolymers (SBR), butadiene-isoprene copolymers (BIR), isoprene-styrene copolymers (SIR) and isoprene-butadiene-styrene copolymers (SBIR).

[0048] In one particular embodiment, the elastomer comprises a styrene-butadiene rubber (SBR). The SBR may have a vinyl content of from about 11 to about 63% by weight. The glass transition temperature of SBR elastomers can range from about  $-10^{\circ}\text{C}$  to about  $-70^{\circ}\text{C}$ .

[0049] In another particular embodiment, the elastomer comprises a butyl rubber either alone or combined with a diene rubber. The butyl rubber may be a butylene polymer or copolymer. For instance, the butylene may be a copolymer of isobutylene and isoprene (IIR). The butyl rubber may also be halogenated as described above. For example, the butyl rubber may be brominated or chlorinated. Examples of butyl rubbers that may be used in the present invention include brominated polyisobutylene isoprene copolymers (BIIR) or brominated isobutylene methyl styrene copolymers (BIMS). One commercially available BIMS elastomer that may be used in accordance with the present invention is EXXPRO available from the Exxon Corporation. Other commercially available butyl rubbers are available from the Bayer Chemical Corporation.

[0050] In addition to the elastomer, the microspheres, the permeability reducing mineral fillers, and the terpene resin, the composition of the present invention can contain various other materials, such as anti-oxidants, accelerators, and processing aids. Further, various other fillers may be incorporated into the composition, such as carbon black or silicas.

[0051] As described above, the terpene resin incorporated into the formulation provides various benefits and advantages. For instance, the resin may improve the processability of the composition as well as actually lower the gas permeability of the composition when formed into a layer or film. Of particular advantage, these benefits are realized without having to incorporate traditional plasticizers into the formulation, such as petroleum based oils. Such plasticizers have been used in the past in order to improve the processability of elastomeric materials. Such plasticizers, however, have an adverse affect on the permeability characteristics of the layer.

[0052] In order to form a barrier layer with the composition described above, the ingredients may be mixed together in a standard mixer, such as a Banbury mixer commercially available from the Farrel Corp. of Ansonia, CT or a Brabender mixer commercially available from C.W. Brabender Instruments Inc. of New Jersey. During the

mixing process, the permeability reducing mineral fillers become intercalated and/or exfoliated in the elastomer and terpene hydrocarbon resin mixture. The exfoliation process produces a good dispersion of the particles with a high aspect ratio. If the microspheres are hollow, it may be advantageous to add them to the mixture later, *e.g.*, in the mill, and take other steps known to those having ordinary skill in the art to minimize the energy imposed on the hollow spheres and thereby prevent their breakage.

[0053] After mixing, the formulation may be formed into a layer or film by processes such as extrusion. If the formulation includes permeability reducing mineral fillers, the film or layer being formed may also be calendered to impart a preferred orientation to the exfoliated particles in the rubber. For instance, if the particles have a plate-like shape, calendering may cause the platelets to orient perpendicular to the direction of gas migration for improving the permeability characteristics of the layer.

[0054] After being formed into a film or layer or while being formed into a film or layer, the composition may then be cured in order to vulcanize the rubber. In one embodiment, the composition may be heated at about 150-160°C for about 30 minutes and at about 16 bars pressure during the curing process. Optimum curing times were determined by a MDR rheometer.

[0055] Barrier layers made according to the present invention may be incorporated into numerous articles. For example, in one embodiment, barrier layers made according to the present invention may be incorporated into elastomeric articles that are intended to be inflated with a gas. In these applications, the barrier layer inhibits gas flow through the wall of the article. Particular examples of articles that may incorporate a barrier layer according to the present invention include sports balls such as footballs, basketballs, and the like, flotation devices such as inflatable boats, air mattresses, and the like.

[0056] FIG. 1 is a cross sectional view of one embodiment of a tire incorporating a barrier layer made according to the present invention. The tire **10** includes a carcass **12** and a tread **14**. The carcass **12** comprises a rubber material and, as shown, has a generally u-shaped cross section. The carcass **12** includes a first side wall **16** and a second side wall **18**. The side walls **16**, **18** are connected to the tread **14** on one end and terminate at an opposite end to form a first bead **20** and a second bead **22**. The beads **20**, **22** are seated in a mounting rim **24**.

[0057] In order to reinforce the tire **10**, the carcass **12** further includes a first bead wire **26** embedded within the first bead **20** and a second bead wire **28** embedded within the second bead **22**. The bead wires **26, 28** can be made from, for instance, metallic wires or cables. A radial carcass reinforcement **30** is wrapped around and anchored by the bead wires **26, 28**. The tire **10** further includes a crown reinforcement **32** that may comprise, for example, a plurality of belts located below the tread **14**. The crown reinforcement **32** may comprise, for example, at least two plies of metallic wires or cables parallel to one another within each ply.

[0058] In accordance with an embodiment of the present invention, the tire **10** further includes a barrier layer **50** that, in this embodiment, forms an inner lining around the interior surface of the tire. The barrier layer **50** inhibits pressurized gases from migrating through the walls of the tire. In particular embodiments, the barrier layer **50** is made from a mixture of an elastomer and permeability reducing particles that include microspheres. When incorporated into a tire as shown in FIG. 1, the barrier layer **50** may have a thickness that varies depending upon the particular application and the type of tire being constructed. For some applications, for example, the barrier layer may have a thickness of less than about 3 mm including, for example, a thickness of between about 0.1 mm and about 3 mm or between about 0.25 mm to about 1.5 mm. It should be understood, however, that in other embodiments, the barrier layer may have a thickness greater than about 3 mm.

[0059] In the embodiment shown in FIG. 1, the barrier layer **50** is positioned on the interior surface of the tire **10**. It should be understood, however, that in other embodiments the barrier layer may be positioned at other locations. For example, alternatively, the barrier layer may be incorporated into the middle of the carcass of the tire **10**.

[0060] In order to form the tire **10** as shown in FIG. 1, any number of conventional processes may be used. In general, the carcass **12** of the tire **10** is made by combining an elastomer, such as a styrene polybutadiene rubber, with various additives in a high shear mixer, such as a Banbury mixer. For example, in one embodiment, approximately 75 to 125 parts of rubber are combined with one or more reinforcing filler, such as carbon black and/or silica. For example, in another embodiment, from about 50 parts to about 70 parts of carbon black and silica are combined with the rubber.

[0061] In addition to the fillers, elemental sulfur and a plasticizer may be combined into the formulation. The sulfur may be present, for instance, in an amount from about 1 to about 15 parts by weight. The plasticizer, which may comprise a hydrocarbon oil, may be present in an amount from about 1 to about 20 parts by weight.

[0062] In addition to the above, various other minor ingredients may be contained in the formulation. For instance, typical rubber formulations further contain an accelerator, an antioxidant, and at least one tackifying resin.

[0063] After the above ingredients are mixed together, the composition is extruded into sheets and calendered. The sheets are then placed in a mold around various reinforcing elements for forming the tire as known to those having ordinary skill in the art.

[0064] The invention is further illustrated by the following examples, which are to be regarded only as illustrations and not delimitative of the invention in any way. The properties of the compositions disclosed in the examples were evaluated as described below.

[0065] Moduli of elongation (MPa) were measured at 10%, 100% and at 300% at a temperature of 23 °C in accordance with ASTM Standard D412 on ASTM C test pieces. These measurements are true secant moduli in MPa, that is to say the secant moduli calculated reduced to the real cross-section of the test piece at the given elongation.

[0066] Hysteresis losses (HL) were measured in percent by rebound at 60 °C at the sixth impact in accordance with the following equation:

$$HL (\%) = 100 (W_0 - W_1)/W_1,$$

where  $W_0$  is the energy supplied and  $W_1$  is the energy restored.

[0067] The elongation property was measured as elongation at break (%) and the corresponding elongation stress (MPa), which is measured at 23 °C in accordance with ASTM Standard D412 on ASTM C test pieces.

[0068] The Modulus Hysteresis (MH) was measured on an Instron Model 55654 tensile tester. The energy loss of applying 100% strain was measured on the sample.

[0069] Gas Permeability was measured using a MOCON OX-TRAN 2/60 permeability tester at 40°C. Cured sample disks of measured thickness (approximately 0.8-1.0 mm) were mounted on the instrument and sealed with vacuum grease. 10 psi of nitrogen was kept on one side of the disk, whereas 10 psi of oxygen was on the other side. Using a



Coulox oxygen detector on the nitrogen side, the increase in oxygen concentration was monitored. The oxygen concentration on the nitrogen side to reach a constant value is recorded and used to determine the oxygen permeability.

#### Example 1

[0070] Elastomer formulations were prepared using the components shown in Table 1 and using procedures well known to one having ordinary skill in the art. The amount of each component making up the elastomer formulations shown in Table 1 are provided in parts per hundred parts by weight (phr) of the elastomer. The curative package included ZnO, sulfur, accelerator and stearic acid.

[0071] The elastomer formulations were prepared by mixing the components given in Table 1, in a Banbury mixer operating at 55-65 RPM until a temperature of between 155 and 170 °C was reached. Vulcanization was effected at 150 °C for 60 minutes. The glass microspheres were hollow glass microspheres, product S60HS, available from 3M. The formulations were then tested to measure their physical properties.

Table 1 - Physical Properties of Elastomers Having Glass Microspheres

<b>Elastomer Composition</b>	<b>E1</b>	<b>E2</b>	<b>E3</b>	<b>E4</b>
Elastomer (BIRR)	100	100	100	100
Glass Microspheres, phr	0	10	20	30
Carbon Black N772, phr	51	51	51	51
Phenolic Tackifier Resin, phr	2.5	2.5	2.5	2.5
Curative, phr	5.7	5.7	5.7	5.7
<b>Measured Properties</b>				
Hysteresis @ 60 °C	31.6	35.3	36.9	38.6
Modulus 10% @ 23 °C (MPa)	2.84	3.17	3.78	4.55
Modulus 100% @ 23 °C (MPa)	0.96	0.95	0.89	0.82
Elongation Strain (%)@ 23 °C	643	502	410	415
% Permeability Change		-36.8	-42.2	-46.0

[0072] Surprisingly, the addition of 10-30 phr of microspheres resulted in a permeability improvement of between 37 and 46% with very minor changes in the other physical properties. It should be noted that while hollow spheres were used in this study, solid spheres are equally suitable. One advantage of using hollow spheres is that, for those embodiments that would find it useful, the density of the elastomer is lowered.

[0073] The terms “comprising,” “including,” and “having,” as used in the claims and specification herein, shall be considered as indicating an open group that may include other elements not specified. The term “consisting essentially of,” as used in the claims and specification herein, shall be considered as indicating a partially open group that may include other elements not specified, so long as those other elements do not materially alter the basic and novel characteristics of the claimed invention. The terms “a,” “an,” and the singular forms of words shall be taken to include the plural form of the same words, such that the terms mean that one or more of something is provided. The terms “at least one” and “one or more” are used interchangeably. The term “one” or “single” shall be used to indicate that one and only one of something is intended. Similarly, other specific integer values, such as “two,” are used when a specific number of things is intended. The terms “preferably,” “preferred,” “prefer,” “optionally,” “may,” and similar terms are used to indicate that an item, condition or step being referred to is an optional (not required) feature of the invention.

[0074] It should be understood from the foregoing description that various modifications and changes may be made to the embodiments of the present invention without departing from its true spirit. The foregoing description is provided for the purpose of illustration only and should not be construed in a limiting sense. Only the language of the following claims should limit the scope of this invention.

CLAIMS

What is claimed is:

1. A pneumatic tire, comprising a barrier layer, the barrier layer comprising:  
an elastomer; and  
between 1 and 50 phr of glass microspheres, ceramic microspheres or combinations thereof.
2. The tire of claim 1, wherein the microspheres are glass.
3. The tire of claim 2, wherein the microspheres have a crush strength of at least 2,000 psi.
4. The tire of claim 1, wherein the microspheres are ceramic.
5. The tire of claim 4, wherein the ceramic microspheres are silica-alumina ceramic microspheres.
6. The tire of claim 1, wherein the microspheres are surface treated to provide a surface comprising a silane coupling agent.
7. The tire of claim 1, wherein the microspheres have a median diameter of between 20 and 40 microns.
8. The tire of claim 1, wherein the elastomer comprises a butyl rubber that is a butylene polymer or copolymer.
9. The tire of claim 8, wherein the elastomer is selected from a copolymer of isobutylene and isoprene, a copolymer of brominated polyisobutylene and isoprene, a copolymer of brominated isobutylene and methyl styrene or combinations thereof.

10. The tire of claim 1, wherein the elastomer comprises a butyl rubber and a diene rubber.
11. The tire of claim 1, wherein the microspheres are hollow.
12. The tire of claim 1, further comprising:
  - a terpene resin having a glass transition temperature greater than about 50°C and a softening point of less than about 170°C.
13. The tire of claim 12, wherein the resin has a glass transition temperature of greater than about 70°C.
14. The tire of claim 12, wherein the resin has a softening point of less than about 140°C.
15. The tire of claim 12, wherein the resin comprises a polylimonene, poly-alpha or beta-pinene, or mixtures thereof.
16. The tire of claim 12, wherein the resin is present in the composition in an amount from about 1 to about 50 phr.
17. The tire of claim 1, further comprising:
  - a permeability reducing mineral filler.
18. An article, comprising a barrier layer, the barrier layer comprising:
  - an elastomer; and
  - between 1 and 50 phr of microspheres having a crush strength of at least 2000 psi.
19. The article of claim 18, wherein the article is an inflatable sport ball.

20. The article of claim 18, wherein the elastomer is selected from a butyl rubber that is a butylene polymer or copolymer, a diene rubber or combinations thereof.

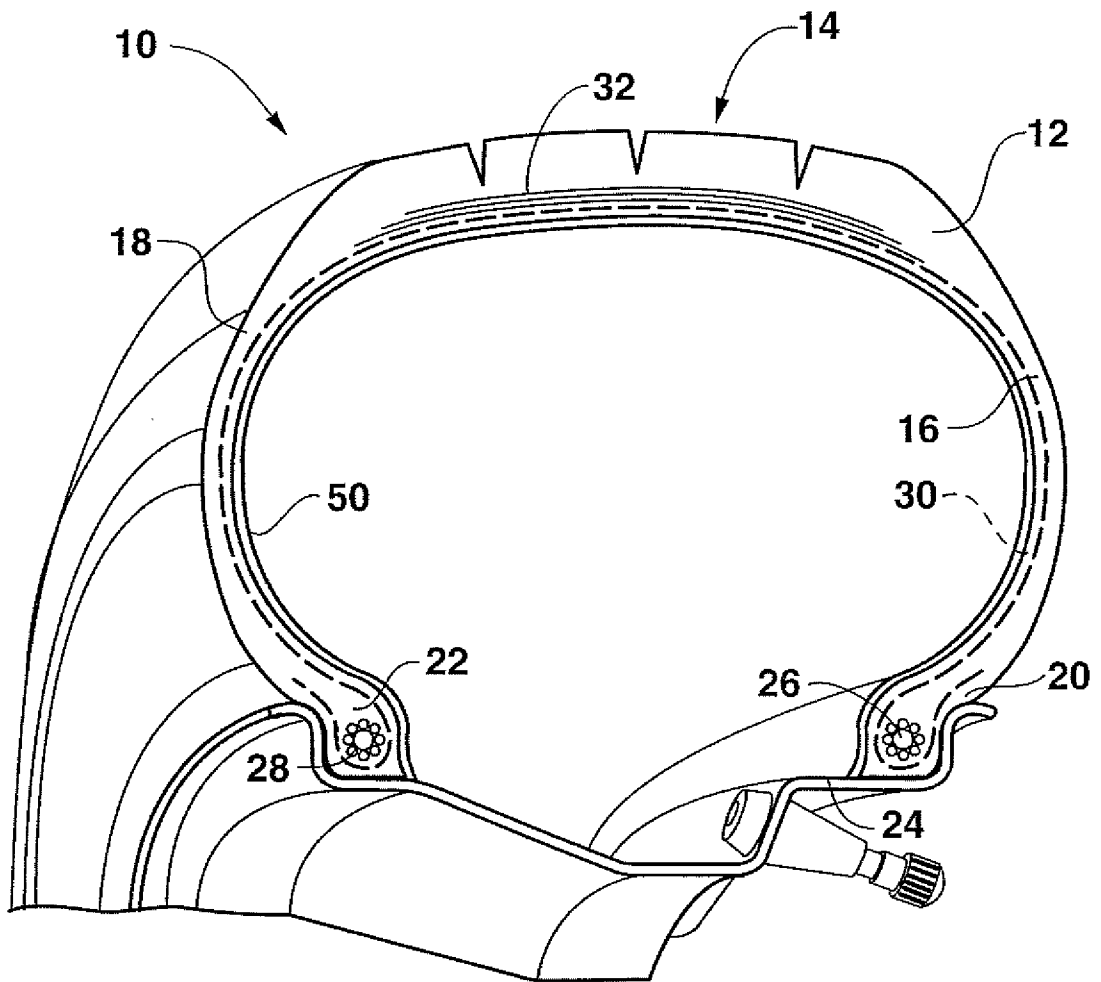


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 07/65344

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B32B 25/00, 33/00 (2007.01)

USPC - 428/406; 523/166

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

USPC - 428/406; 523/166

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
USPC - 427/215,393.6; 428/325,404,406,912; 523/166,219 (text search - see search terms below)

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

PubWEST (PGPB,USPT,USOC,EPAB,JPAB);DialogPro (General Research); Google Scholar

Tire, ball, barrier, elastomer, phr, %, percent, glass, ceramic, microsphere, strength, psi, silica, alumina, silane, diameter, microns, butyl rubber, butylene, isobutylene, isoprene, methyl styrene, brominated, diene, terpene, filler

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	US 6,962,181 B2 (DEEVERS et al.) 08 November 2005 (08.11.2005), abstract, col 1, ln 6-28, col 2, ln 5-8, col 2, ln 35 - col 3, ln 20, col 3, ln 35-47, col 3, ln 63-67, col 6, ln 29-35 and col 8, ln 3-10.	1-3, 7-11, 18 and 20 ----- 4-6, 12-17 and 19
Y	WO 2006/047509 A2 (BERGMAN) 04 May 2006 (04.05.2006), abstract, para [0001], [0007], [0008], [0010], [0013], [0022]-[0028], [0046], [0051], [0062] and [0064].	12-17 and 19
Y	JP 10-087890 A (JALICS et al.) 07 April 1998 (07.04.1998), abstract.	4-6
Y	US 4,273,806 A (STECHLER) 16 June 1981 (16.06.1981), abstract, col 2, ln 55-60, col 3, ln 1-5, col 3, ln 24-35 and col 4, ln 1-28.	5
A	US 2006/0233972 A1 (MURAMATSU et al.) 19 October 2006 (19.10.2006), entire document.	5
A	US 5,925,702 A (HECKER et al.) 20 July 1999 (20.07.1999), entire document	1-20

Further documents are listed in the continuation of Box C.

\* Special categories of cited documents:

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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

"&" document member of the same patent family

Date of the actual completion of the international search

19 September 2007

Date of mailing of the international search report

05 NOV 2007

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