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(54) Title: LOW PERMEABILITY NANOCOMPOSITES

(57) Abrégé/Abstract:

The present invention includes blends of a halogenated elastomer such as a butyl rubber or an interpolymer of, on one embodiment, a C₄ to C₇ isomonoolefin, a para-methylstyrene and a para-(halomethylstyrene), the interpolymer having been pre-mixed with an exfoliating compound and clay, the entire blend forming a nanocomposite in one embodiment. The clay may or may not have undergone an additional exfoliating treatment prior to blending with the halogenated elastomer. The interpolymer/clay mixture forms a distinct phase in the nanocomposite blend of the invention. The blend of the invention has improved air barrier properties and is suitable as an air barrier.

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(54) Title: LOW PERMEABILITY NANOCOMPOSITES

(57) Abstract: The present invention includes blends of a halogenated elastomer such as a butyl rubber or an interpolymer of, on one embodiment, a C₄ to C₇ isomonoolefin, a para-methylstyrene and a para-(halomethylstyrene), the interpolymer having been pre-mixed with an exfoliating compound and clay, the entire blend forming a nanocomposite in one embodiment. The clay may or may not have undergone an additional exfoliating treatment prior to blending with the halogenated elastomer. The interpolymer/clay mixture forms a distinct phase in the nanocomposite blend of the invention. The blend of the invention has improved air barrier properties and is suitable as an air barrier.

TITLE: LOW PERMEABILITY NANOCOMPOSITES**FIELD OF THE INVENTION**

The present invention provides a low-permeability nanocomposite useful for air barriers which is a blend of an elastomer, vulcanized or unvulcanized, a nano-filler such as a clay, and an exfoliating additive including long-chain tertiary amines.

BACKGROUND

Nanocomposites are polymer systems containing inorganic particles with at least one dimension in the nanometer range. Some examples of these are disclosed in US 6,060,549, 6,103,817, 6,034,164, 5,973,053, 5,936,023, 5,883,173, 5,807,629, 5,665,183, 5,576,373, and 5,576,372. A common type of inorganic particle used in nanocomposites are phyllosilicates, an inorganic substance from the general class of so called "nano-clays" or "clays". Ideally, intercalation should take place in the nanocomposite, wherein the polymer inserts into the space or gallery between the clay surfaces. Ultimately, it is desirable to have exfoliation, wherein the polymer is fully dispersed with the individual nanometer-size clay platelets. Due to the general enhancement in air barrier qualities of various polymer blends when clays are present, there is a desire to have a nanocomposite with low air permeability; especially a dynamically vulcanized thermoplastic nanocomposite such as used in the manufacture of tires.

The preparation of elastomer-clay nanocomposites uses a number of methods to generate exfoliated clays. One of the most common methods relies upon the use of organically modified montmorillonite clays. Organoclays are produced through solution based ion-exchange reactions that replace sodium ions that exist on the surface of sodium montmorillonite with alkyl or aryl ammonium compounds. One of the deficiencies of this method is the limited thermal stability of the amines. A second is the lack of chemical bonding with the matrix, often

leading to poor mechanical properties and increased hysteresis. A third is the negative impact that the release amines and degradation products have on the transport properties.

5 One method to improve the organoclay performance is to use functionalized polymers to treat the clay. This approach has been limited to materials that are soluble in water or to materials that can be incorporated into the polymerization reaction. This approach has been used to prepare nylon nanocomposites, using for example, oligomeric and monomeric caprolactam as 10 the modifier. Polyolefin nanocomposites have utilized maleic anhydride grafted polyolefins to achieve some success in the formation of nanocomposites.

15 For example, it is known to utilize exfoliated-clay filled nylon as a high impact plastic matrix, such as disclosed in US 6,060,549 to *Li et al.* In particular, *Li et al.* disclose a blend of a thermoplastic resin such as nylon and a copolymer of a C₄ to C₇ isomonoolefin and a para-methylstyrene and a para-(halomethylstyrene), the blend also including nylon containing exfoliated-clays 20 that are used as a high impact material. Further, Japanese Unexamined Application P2000-160024 to *Yuichi et al.* discloses a thermoplastic elastomer composition which can be used as an air barrier. The nanocomposite in *Yuichi et al.* includes a blend similar to that disclosed in *Li et al.*

25 Nanocomposites have also been formed using brominated copolymers of isobutylene and para-methylstyrene. See, for example, *Elspass et. al.*, US 5,807,629, US 5,883,173, and US 6,034,164. It has been found that the efficiency of clay exfoliation is increased by increasing bromination level. Unfortunately these copolymers are very reactive and it is difficult to achieve high levels of functionalization without undue added vulcanization. Optimal performance in many applications requires the minimum level of vulcanization that yields 30 acceptable physical properties, in that way aging and durability are maximized.

Thus, there is still a problem of achieving a nanocomposite suitable for an air barrier, in particular, an air barrier incorporating the copolymer (or "interpolymer") of a C₄ to C₇ isomonoolefin and a para-methylstyrene and a para-(halomethylstyrene). While enhancing the impact properties and abrasion resistance of plastics such as polyamides, this copolymer tends to be a poor air barrier as compared with that of polyamide alone or other low-permeability plastic matrices. What is needed is an exfoliated nanocomposite of a halogenated copolymer of a C₄ to C₇ isomonoolefin, a para-methylstyrene and a para-(halomethylstyrene).

SUMMARY OF THE INVENTION

An embodiment of the present invention includes a nanocomposite including halogenated elastomers such as, for example, interpolymers of C₄ to C₇ isomonoolefin, a para-methylstyrene and a para-(halomethylstyrene) that have low levels of reactive bromide but which are activated toward the formation of an exfoliated nanocomposite through the addition of a functionalized additive. Alternately the copolymer may be selected with higher levels of bromination and then some fraction of these sites are complexed with the additive thereby reducing their reactivity in vulcanization. In another embodiment, the nanocomposite includes halogenated elastomers comprising C₄ to C₇ isoolefin derived units, multiolefin derived units, and halogenated multiolefin derived units, or "halogenated butyl" rubber. The additive should be capable of reaction with the halogen sites on the polymer to form complexes which help exfoliate the clay. The clay may be exfoliated prior to mixing with the interpolymer in one embodiment, and ion exchanged with a counterion in another embodiment.

An embodiment of the invention includes a nanocomposite useful for air barriers which includes a clay, an interpolymer or halogenated butyl rubber, an exfoliating additive, and optionally a polyfunctional curative, the exfoliating agent

being an amine having the structure $R^2R^3R^4N$, wherein R^2 , R^3 , and R^4 are C_1 to C_{20} alkyls or alkenes which may be the same or different. The interpolymer is a copolymer of C_4 to C_7 isomonoolefin derived units, a para-methylstyrene derived units and a para-(halomethylstyrene) derived units, wherein the para-(halomethylstyrene) derived units are present from 0.4 to 1 mol% in the interpolymer. In one embodiment, the amine is a tertiary amine, and at least R_1 is a C_{14} to C_{20} alkyl or alkene. The exfoliating agent may be selected from the group consisting of N,N-dimethyl-octadecylamine, N,N-dioctadecyl-methylamine, dihydrogenated tallowalkyl-methylamine, amine-terminated polytetrahydrofuran and mixtures thereof. Further, the exfoliating agent may be a thiosulfate compound such as hexamethylene sodium thiosulfate. The nanocomposite may also include a filler such as carbon black. The clay can be untreated sodium montmorillonite or a traditional organically modified clay.

15 DETAILED DESCRIPTION OF THE INVENTION

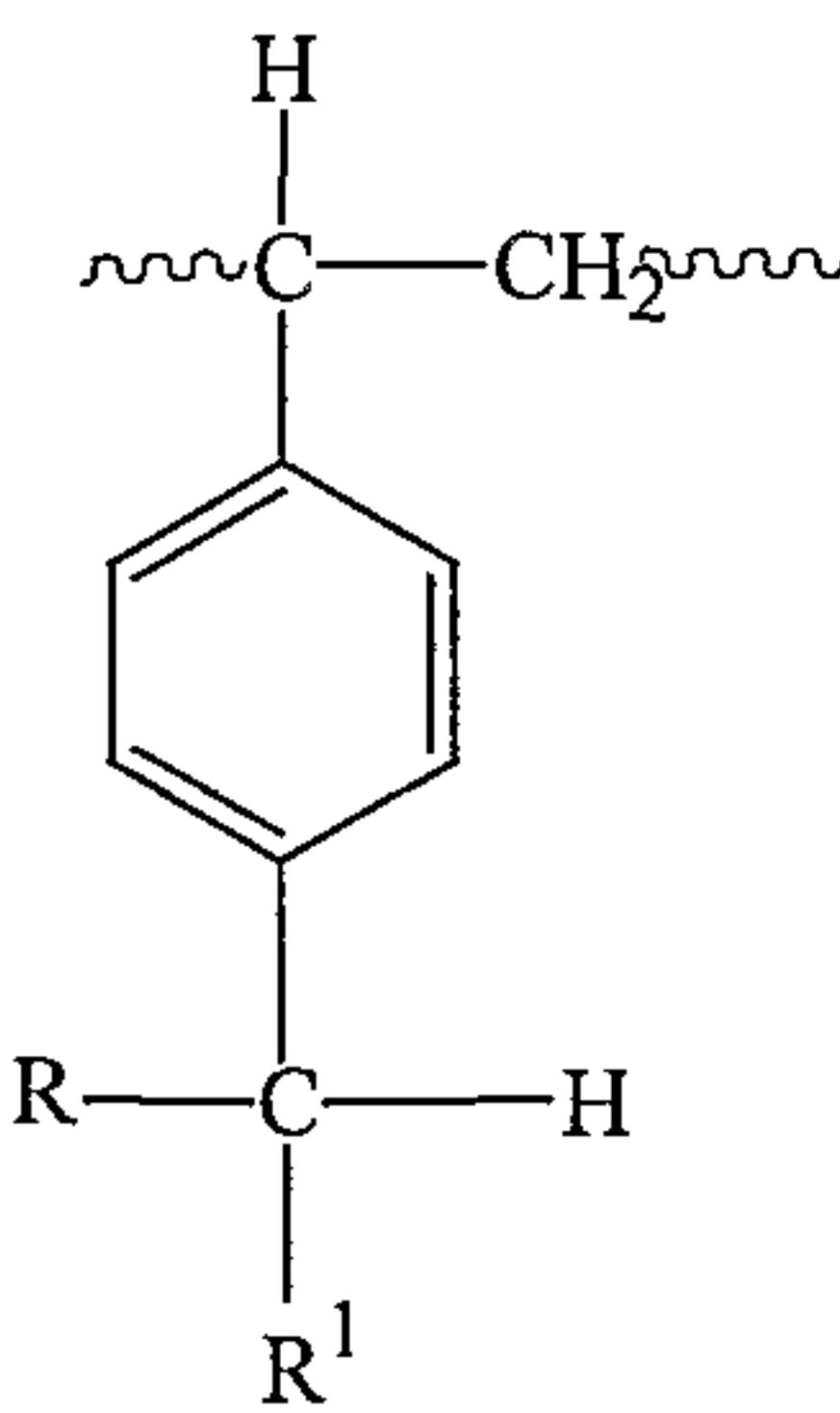
The present invention includes nanocomposite compositions of halogenated elastomers and clays treated with one or more exfoliating additives. The invention is not herein limited to the order of addition of the components. The halogenated elastomer may be an interpolymer comprises C_4 to C_7 isoolefin derived units, para-methylstyrene derived units and a para-(halomethylstyrene) derived units in one embodiment, and comprises C_4 to C_7 isoolefin derived units, multiolefin derived units, and halogenated multiolefin derived units in another embodiment. The nanocomposite can also include other cross-linking agents, thermoplastics, and secondary rubbers or "general purpose rubbers" as described herein.

25 Halogenated Elastomer

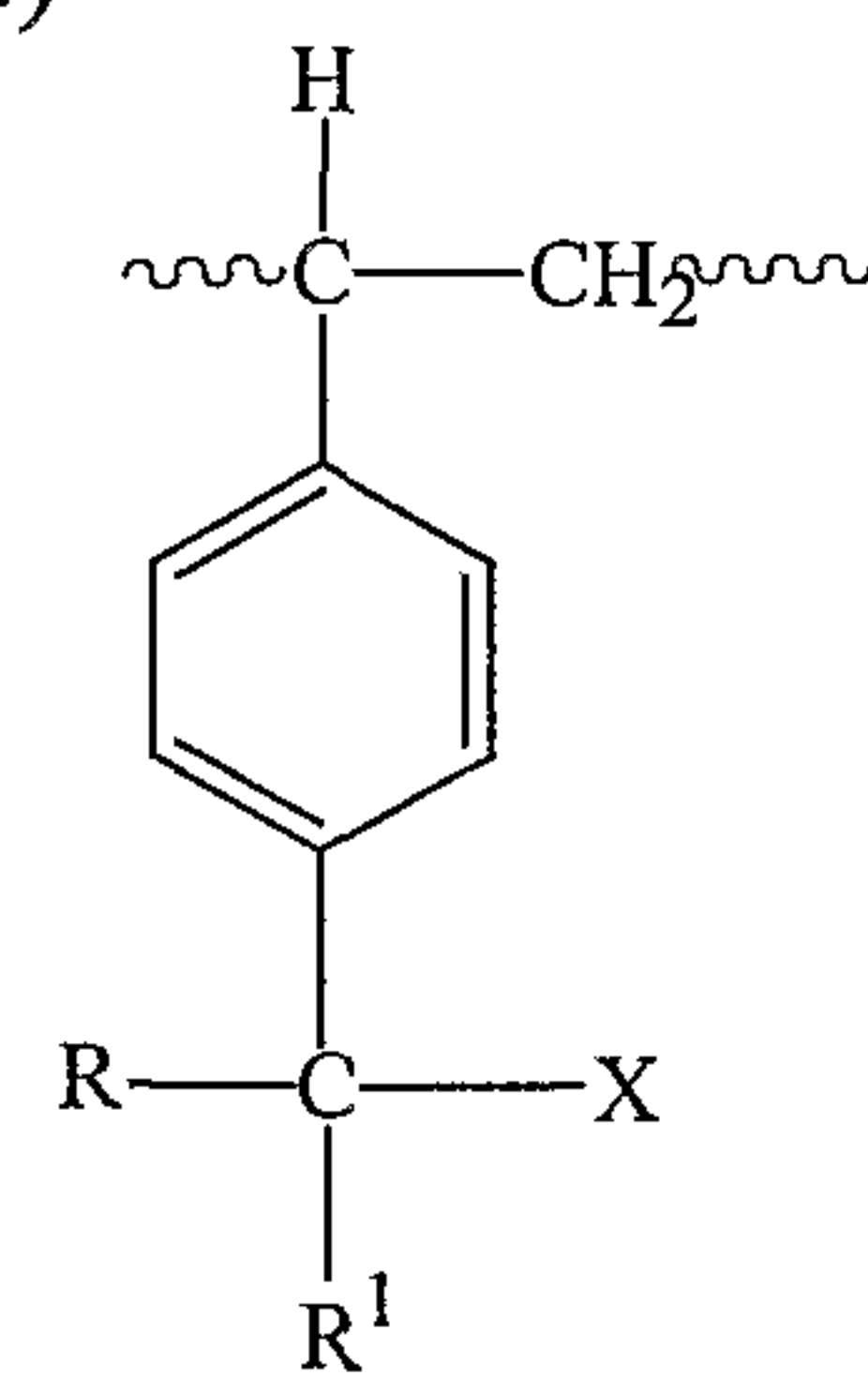
The interpolymers in one embodiment of the invention are random elastomeric copolymers of a C_4 to C_7 isomonoolefin, such as isobutylene and a para-alkylstyrene comonomer, preferably para-methylstyrene containing at least

80%, more preferably at least 90% by weight of the para-isomer and also include functionalized interpolymers wherein at least some of the alkyl substituents groups present in the styrene monomer units contain benzylic halogen or some other functional group. In another embodiment of the invention, the interpolymer 5 is a random elastomeric copolymer of ethylene or a C₃ to C₆ α -olefin and a para-alkylstyrene comonomer, preferably para-methylstyrene containing at least 80%, more preferably at least 90% by weight of the para-isomer and also include functionalized interpolymers wherein at least some of the alkyl substituents groups present in the styrene monomer units contain benzylic halogen or some 10 other functional group. Preferred materials may be characterized as interpolymers containing the following monomer units randomly spaced along the polymer chain:

(1)



(2)



15 wherein R and R¹ are independently hydrogen, lower alkyl, preferably C₁ to C₇, alkyl and primary or secondary alkyl halides and X is a functional group such as halogen. Preferably R and R¹ are each hydrogen. Up to 60 mol% of the para-substituted styrene present in the interpolymer structure may be the functionalized structure (2) above in one embodiment, and in another embodiment from 0.1 to 5 mol%. In yet another embodiment, the amount of functionalized structure (2) is 20 from 0.4 to 1 mol%.

The functional group X may be halogen or some other functional group which may be incorporated by nucleophilic substitution of benzylic halogen with other groups such as carboxylic acids; carboxy salts; carboxy esters, amides and imides; hydroxy; alkoxide; phenoxide; thiolate; thioether; xanthate; cyanide; cyanate; amino and mixtures thereof. These functionalized isomonoolefin copolymers, their method of preparation, methods of functionalization, and cure are more particularly disclosed in US 5,162,445.

Most useful of such functionalized materials are elastomeric random interpolymers of isobutylene and para-methylstyrene containing from 0.5 to 20 mol% para-methylstyrene wherein up to 60 mol% of the methyl substituent groups present on the benzyl ring contain a bromine or chlorine atom, preferably a bromine atom (para-(bromomethylstyrene)), as well as acid or ester functionalized versions thereof.

In a preferred embodiment, the functionality is selected such that it can react or form polar bonds with functional groups present in the matrix polymer, for example, acid, amino or hydroxyl functional groups, when the polymer components are mixed at high temperatures.

These functionalized interpolymers have a substantially homogeneous compositional distribution such that at least 95% by weight of the polymer has a para-alkylstyrene content within 10% of the average para-alkylstyrene content of the polymer. Desirable interpolymers are also characterized by a narrow molecular weight distribution (M_w/M_n) of less than 5, more preferably less than 2.5, a preferred viscosity average molecular weight in the range of from 200,000 up to 2,000,000 and a preferred number average molecular weight in the range of from 25,000 to 750,000 as determined by gel permeation chromatography.

The interpolymers may be prepared by a slurry polymerization of the monomer mixture using a Lewis acid catalyst, followed by halogenation, preferably bromination, in solution in the presence of halogen and a radical initiator such as heat and/or light and/or a chemical initiator and, optionally, followed by electrophilic substitution of bromine with a different functional moiety.

Preferred BIMS polymers are brominated polymers that generally contain from 0.1 to 5% mole of bromomethylstyrene groups relative to the total amount of monomer derived units in the polymer. In another embodiment, the amount of bromomethyl groups is from 0.2 to 3.0 mol%, and from 0.3 to 2.8 mol% in yet another embodiment, and from 0.4 to 2.5 mol% in yet another embodiment, and from 0.3 to 2.0 in yet another embodiment, wherein a desirable range may be any combination of any upper limit with any lower limit. Expressed another way, preferred copolymers contain from 0.2 to 10 wt% of bromine, based on the weight of the polymer, from 0.4 to 6 wt% bromine in another embodiment, and from 0.6 to 5.6 wt% in another embodiment, are substantially free of ring halogen or halogen in the polymer backbone chain. In one embodiment of the invention, the interpolymers are a copolymer of C₄ to C₇ isoolefin derived units (or isomonoolefin), para-methylstyrene derived units and para-(halomethylstyrene) derived units, wherein the para-(halomethylstyrene) units are present in the interpolymers from 0.4 to 3.0 mol% based on the total number of para-methylstyrene, and wherein the para-methylstyrene derived units are present from 3 wt% to 15 wt% based on the total weight of the polymer in one embodiment, and from 4 wt% to 10 wt% in another embodiment. In another embodiment, the para-(halomethylstyrene) is para-(bromomethylstyrene).

The nanocomposite of the present invention may also include a halogenated butyl rubber component, either with the interpolymers or as the only elastomer combined with the exfoliated clay. In one embodiment of the invention,

the halogenated rubber component is a halogenated copolymer of a C₄ to C₆ isooolefin and a multiolefin. In another embodiment, the halogenated rubber component is a blend of a polydiene or block copolymer, and a copolymer of a C₄ to C₆ isooolefin and a conjugated, or a "star-branched" butyl polymer. The halogenated butyl polymer useful in the present invention can thus be described as a halogenated elastomer comprising C₄ to C₇ isooolefin derived units, multiolefin derived units, and halogenated multiolefin derived units, and includes both "halogenated butyl rubber" and so called "halogenated star-branched" butyl rubber.

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In one embodiment, the halogenated butyl rubber is brominated butyl rubber, and in another embodiment is chlorinated butyl rubber. General properties and processing of halogenated butyl rubbers is described in THE VANDERBILT RUBBER HANDBOOK 105-122 (Robert F. Ohm ed., R.T. Vanderbilt Co., Inc. 1990), and in RUBBER TECHNOLOGY 311-321 (Maurice Morton ed., Chapman & Hall 1995). Butyl rubbers, halogenated butyl rubbers, and star-branched butyl rubbers are described by *Edward Kresge and H.C. Wang* in 8 KIRK-OTHMER ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY 934-955 (John Wiley & Sons, Inc. 4th ed. 1993).

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The halogenated rubber component of the present invention includes, but is not limited to, brominated butyl rubber, chlorinated butyl rubber, star-branched polyisobutylene rubber, star-branched brominated butyl (polyisobutylene/isoprene copolymer) rubber; isobutylene-bromomethylstyrene copolymers such as isobutylene/meta-bromomethylstyrene, isobutylene/para-bromomethylstyrene, isobutylene/chloromethylstyrene, halogenated isobutylene cyclopentadiene, and isobutylene/para-chloromethylstyrene, and the like halomethylated aromatic interpolymers as in US 4,074,035 and US 4,395,506; isoprene and halogenated isobutylene copolymers, polychloroprene, and the like, and mixtures of any of the

above. Some embodiments of the halogenated rubber component are also described in US 4,703,091 and 4,632,963.

More particularly, in one embodiment of the brominated rubber component of the invention, a halogenated butyl rubber is used. As used herein, "halogenated butyl rubber" refers to both butyl rubber and so-called "star-branched" butyl rubber, described below. The halogenated butyl rubber is produced from the halogenation of butyl rubber. Preferably, the olefin polymerization feeds employed in producing the halogenated butyl rubber of the invention are those olefinic compounds conventionally used in the preparation of butyl-type rubber polymers. The butyl polymers are prepared by reacting a comonomer mixture, the mixture having at least (1) a C₄ to C₆ isoolefin monomer component such as isobutylene with (2) a multiolefin, or conjugated diene, monomer component. The isoolefin is in a range from 70 to 99.5 wt% by weight of the total comonomer mixture in one embodiment, and 85 to 99.5 wt% in another embodiment. The conjugated diene component in one embodiment is present in the comonomer mixture from 30 to 0.5 wt% in one embodiment, and from 15 to 0.5 wt% in another embodiment. In yet another embodiment, from 8 to 0.5 wt% of the comonomer mixture is conjugated diene.

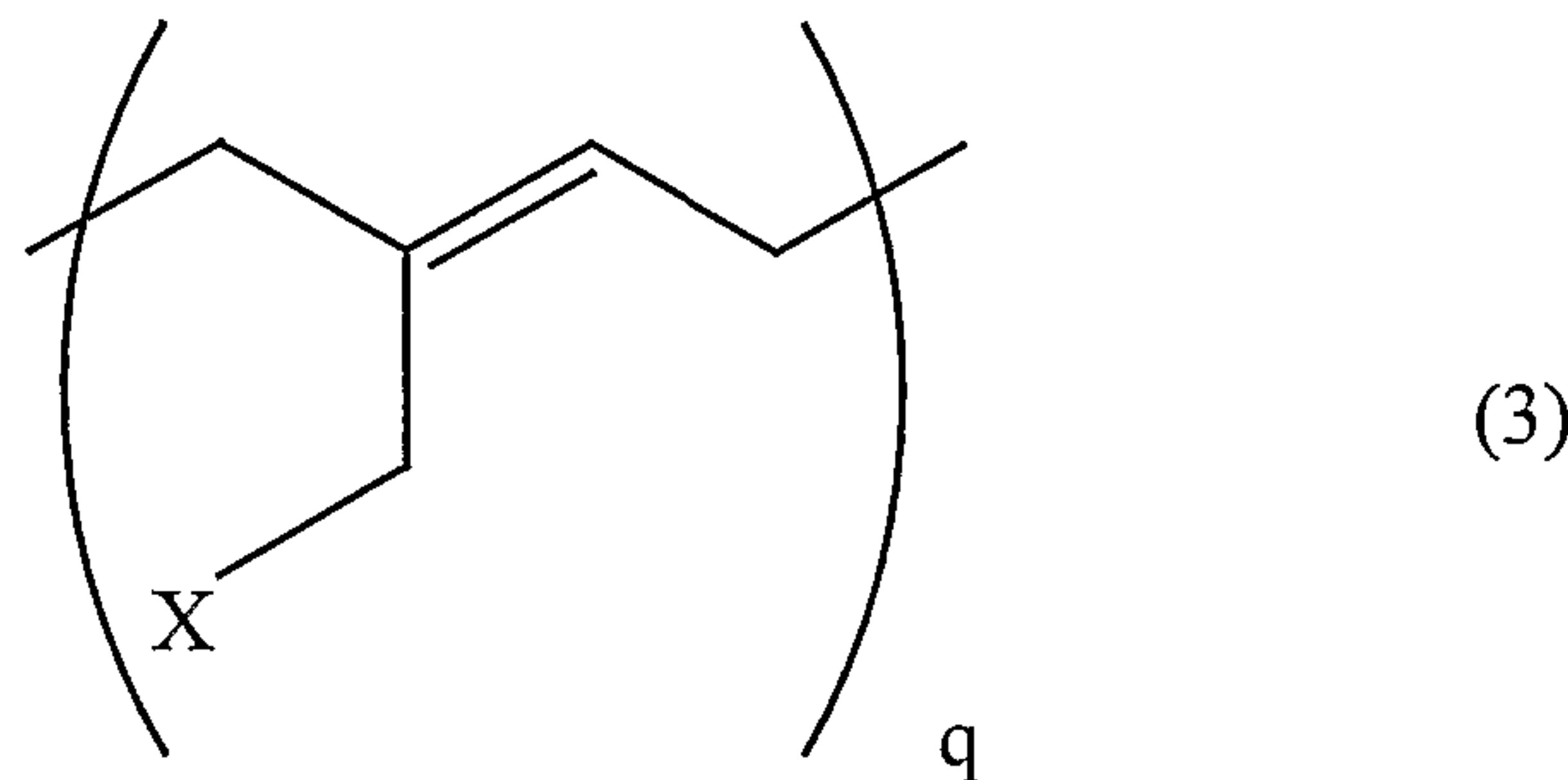
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The isoolefin is a C₄ to C₆ compound such as isobutylene, isobutene 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, and 4-methyl-1-pentene. The multiolefin is a C₄ to C₁₄ conjugated diene such as isoprene, butadiene, 2,3-dimethyl-1,3-butadiene, myrcene, 6,6-dimethyl-fulvene, cyclopentadiene, hexadiene and piperylene. One embodiment of the butyl rubber polymer of the invention is obtained by reacting 92 to 99.5 wt% of isobutylene with 0.5 to 8 wt% isoprene, or reacting 95 to 99.5 wt% isobutylene with from 0.5 wt% to 5.0 wt% isoprene in yet another embodiment.

Halogenated butyl rubber is produced by the halogenation of the butyl rubber product described above. Halogenation can be carried out by any means, and the invention is not herein limited by the halogenation process. Methods of halogenating polymers such as butyl polymers are disclosed in US 2,631,984, 5 3,099,644, 4,554,326, 4,681,921, 4,650,831, 4,384,072, 4,513,116 and 5,681,901. In one embodiment, the halogen is in the so called II and III structures as discussed in, for example, RUBBER TECHNOLOGY at 298-299 (1995). In one embodiment, the butyl rubber is halogenated in hexane diluent at from 40 to 60°C 10 using bromine (Br₂) or chlorine (Cl₂) as the halogenation agent. The halogenated butyl rubber has a Mooney Viscosity of from 20 to 70 (ML 1+8 at 125°C) in one embodiment, and from 25 to 55 in another embodiment. The halogen wt% is from 0.1 to 10 wt% based in on the weight of the halogenated butyl rubber in one embodiment, and from 0.5 to 5 wt% in another embodiment. In yet another embodiment, the halogen wt% of the halogenated butyl rubber is from 1 to 2.2 15 wt%.

In another embodiment, the halogenated butyl or star-branched butyl rubber may be halogenated such that the halogenation is in the primary allylic position. This is typically achieved by such means as free radical bromination or 20 free radical chlorination, or by such methods as secondary treatment halogenated rubbers, such as by heating the rubber, to form the allylic halogenated butyl and star-branched butyl rubber. Common methods of forming the allylic halogenated polymer are disclosed by *Gardner et al.* in US 4,632,963; US 4,649,178; US 4,703,091. Thus, in one embodiment of the invention, the halogenated butyl 25 rubber is such that the halogenated multiolefin units are primary allylic halogenated units, and wherein the primary allylic configuration is present to at least 20 mol% (relative to the total amount of halogenated multiolefin) in one embodiment, and at least 30 mol% in another embodiment. This arrangement can be described as follows (3), wherein X is a halogen, desirably chlorine or bromine, 30 and q is at least mol% based on the total moles of halogen in one embodiment, and

at least 30 mole% in another embodiment, and from 25 mol% to 90 mol% in yet another embodiment:



5 A commercial embodiment of the halogenated butyl rubber of the present invention is Bromobutyl 2222 (ExxonMobil Chemical Company). Its Mooney Viscosity is from 27 to 37 (ML 1+8 at 125°C, ASTM 1646, modified), and the bromine content is from 1.8 to 2.2 wt% relative to the Bromobutyl 2222. Further, cure characteristics of Bromobutyl 2222 are as follows: MH is from 28 to 40 10 dN·m, ML is from 7 to 18 dN·m (ASTM D2084, modified). Another commercial embodiment of the halogenated butyl rubber is Bromobutyl 2255 (ExxonMobil Chemical Company). Its Mooney Viscosity is from 41 to 51 (ML 1+8 at 125°C, ASTM 1646, modified), and the bromine content is from 1.8 to 2.2 wt%. Further, cure characteristics of Bromobutyl 2255 are as follows: MH is from 34 to 48 15 dN·m, ML is from 11 to 21 dN·m (ASTM D2084, modified). The invention is not limited to the commercial source of any of the halogenated rubber components.

20 In another embodiment of the brominated rubber component of the invention, a branched or "star-branched" halogenated butyl rubber is used. In one embodiment, the star-branched halogenated butyl rubber ("SBHR") is a composition of a butyl rubber, either halogenated or not, and a polydiene or block copolymer, either halogenated or not. The halogenation process is described in detail in US 4,074,035, 5,071,913, 5,286,804, 5,182,333 and 6,228,978. The invention is not limited by the method of forming the SBHR. The polydienes/block copolymer, or branching agents (hereinafter "polydienes"), are 25

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typically cationically reactive and are present during the polymerization of the butyl or halogenated butyl rubber, or can be blended with the butyl or halogenated butyl rubber to form the SBHR. The branching agent or polydiene can be any suitable branching agent, and the invention is not limited to the type of polydiene used to make the SBHR.

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In one embodiment, the SBHR is typically a composition of the butyl or halogenated butyl rubber as described above and a copolymer of a polydiene and a partially hydrogenated polydiene selected from the group including styrene, polybutadiene, polyisoprene, polypiperylene, natural rubber, styrene-butadiene rubber, ethylene-propylene diene rubber, styrene-butadiene-styrene and styrene-isoprene-styrene block copolymers. These polydienes are present, based on the monomer wt%, greater than 0.3 wt% in one embodiment, and from 0.3 to 3 wt% in another embodiment, and from 0.4 to 2.7 wt% in yet another embodiment.

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A commercial embodiment of the SBHR of the present invention is Bromobutyl 6222 (ExxonMobil Chemical Company), having a Mooney Viscosity (ML 1+8 at 125°C, ASTM 1646, modified) of from 27 to 37, and a bromine content of from 2.2 to 2.6 wt% relative to the SBHR. Further, cure characteristics of Bromobutyl 6222 are as follows: MH is from 24 to 38 dN·m, ML is from 6 to 16 dN·m (ASTM D2084, modified).

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The halogenated rubber component is present in the blend of the invention from 10 to 90 phr in one embodiment, from 20 to 80 phr in another embodiment, and from 30 to 70 phr in yet another embodiment, wherein a desirable range may be any combination of any upper phr limit with any lower phr limit.

Clay

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Compositions of the invention include at least one interpolymer or halogenated butyl rubber as described above blended by any suitable means with

at least one swellable clay, either pre-mixed with an exfoliating additive or not. Swellable layered clay materials suitable for the purposes of this invention include natural or synthetic phyllosilicates, particularly smectic clays such as montmorillonite, nontronite, beidellite, volkonskoite, laponite, hectorite, saponite, saucomite, magadite, kenyaite, stevensite and the like, as well as vermiculite, halloysite, aluminite oxides, hydrotalcite and the like. These layered clays generally comprise particles containing a plurality of silicate platelets having a thickness of 8-12 \AA tightly bound together at interlayer spacings of 4 \AA or less, and contain exchangeable cations such as Na^+ , Ca^{+2} , K^+ or Mg^{+2} present at the interlayer surfaces.

The layered clay may be intercalated and exfoliated by treatment with organic molecules (swelling or exfoliating "agents" or "additives") capable of undergoing ion exchange reactions with the cations present at the interlayer surfaces of the layered silicate. Suitable exfoliating additives include cationic surfactants such as ammonium, alkylamines or alkylammonium (primary, secondary, tertiary and quaternary), phosphonium or sulfonium derivatives of aliphatic, aromatic or arylaliphatic amines, phosphines and sulfides. Desirable amine compounds (or the corresponding ammonium ion) are those with the structure $\text{R}^2\text{R}^3\text{R}^4\text{N}$, wherein R^2 , R^3 , and R^4 are C_1 to C_{30} alkyls or alkenes in one embodiment, C_1 to C_{20} alkyls or alkenes in another embodiment, which may be the same or different. In one embodiment, the exfoliating agent is a so called long chain tertiary amine, wherein at least R^2 is a C_{14} to C_{20} alkyl or alkene.

Another class of exfoliating additives include those which can be covalently bonded to the interlayer surfaces. These include polysilanes of the structure $-\text{Si}(\text{R}^5)_2\text{R}^6$ where R^5 is the same or different at each occurrence and is selected from alkyl, alkoxy or oxysilane and R^6 is an organic radical compatible with the matrix polymer of the composite.

Other suitable exfoliating additives include protonated amino acids and salts thereof containing 2-30 carbon atoms such as 12-aminododecanoic acid, epsilon-caprolactam and like materials. Suitable swelling agents and processes for intercalating layered silicates are disclosed in US 4,472,538, 4,810,734, 4,889,885 as well as WO92/02582.

In a preferred embodiment of the invention, the exfoliating additive or additives are capable of reaction with the halogen sites on the interpolymer to form complexes which help exfoliate the clay. In one embodiment, the additive includes all primary, secondary and tertiary amines and phosphines; alkyl and aryl sulfides and thiols; and their polyfunctional versions. Desirable additives include: long-chain tertiary amines such as N,N-dimethyl-octadecylamine, N,N-dioctadecyl-methylamine, so called dihydrogenated tallowalkyl-methylamine and the like, and amine-terminated polytetrahydrofuran; long-chain thiol and thiosulfate compounds like hexamethylene sodium thiosulfate.

The exfoliating additive such as described herein is present in the composition in an amount to achieve optimal air retention as measured by the permeability testing described herein. For example, the additive may be present from 0.1 to 20 phr in one embodiment, and from 0.2 to 15 phr in yet another embodiment, and from 0.3 to 10 phr in yet another embodiment. The exfoliating additive may be added to the composition at any stage; for example, the additive may be added to the interpolymer, followed by addition of the clay, or may be added to the interpolymer and clay mixture; or the additive may be first blended with the clay, followed by blending with the interpolymer in yet another embodiment.

In another embodiment of the invention, improved interpolymer impermeability is achieved by the presence of at least one polyfunctional curative. An embodiment of such polyfunctional curatives can be described by the formula

Z--R⁷--Z', wherein R⁷ is one of a C₁ to C₁₅ alkyl, C₂ to C₁₅ alkenyl, and C₆ to C₁₂ cyclic aromatic moiety, substituted or unsubstituted; and Z and Z' are the same or different and are one of a thiosulfate group, mercapto group, aldehyde group, carboxylic acid group, peroxide group, alkenyl group, or other similar group that is capable of crosslinking, either intermolecularly or intramolecularly, one or more strands of a polymer having reactive groups such as unsaturation. So-called bis-thiosulfate compounds are an example of a desirable class of polyfunctional compounds included in the above formula. Non-limiting examples of such polyfunctional curatives are as hexamethylene bis(sodium thiosulfate) and hexamethylene bis(cinnamaldehyde), and others are well known in the rubber compounding arts. These and other suitable agents are disclosed in, for example, the BLUE BOOK, MATERIALS, COMPOUNDING INGREDIENTS, MACHINERY AND SERVICES FOR RUBBER (Don. R. Smith, ed., Lippincott & Petto Inc. 2001). The polyfunctional curative, if present, may be present in the composition from 0.1 to 8 phr in one embodiment, and from 0.2 to 5 phr in yet another embodiment.

Treatment with the swelling agents described above results in intercalation or "exfoliation" of the layered platelets as a consequence of a reduction of the 20 ionic forces holding the layers together and introduction of molecules between layers which serve to space the layers at distances of greater than 4 \AA , preferably greater than 9 \AA . This separation allows the layered silicate to more readily sorb polymerizable monomer material and polymeric material between the layers and facilitates further delamination of the layers when the intercalate is shear mixed with matrix polymer material to provide a uniform dispersion of the exfoliated 25 layers within the polymer matrix.

The amount of clay or exfoliated clay incorporated in the nanocomposites in accordance with an embodiment of the invention is sufficient to develop an improvement in the mechanical properties or barrier properties of the nanocomposite, for example, tensile strength or oxygen permeability. Amounts

generally will range from 0.5 to 10 wt% in one embodiment, and from 1 to 5 wt% in another embodiment, based on the polymer content of the nanocomposite. Expressed in parts per hundred rubber, the clay or exfoliated clay may be present from 1 to 30 phr in one embodiment, and from 5 to 20 phr in another embodiment. In one embodiment, the exfoliated clay is an alkylamine-exfoliated clay.

Secondary Rubber Component

A secondary rubber, or "general purpose rubber" component may be present in compositions and end use articles of the present invention. These rubbers include, but are not limited to, natural rubbers, polyisoprene rubber, poly(styrene-*co*-butadiene) rubber (SBR), polybutadiene rubber (BR), poly(isoprene-*co*-butadiene) rubber (IBR), styrene-isoprene-butadiene rubber (SIBR), ethylene-propylene rubber (EPM), ethylene-propylene-diene rubber (EPDM), polysulfide, nitrile rubber, propylene oxide polymers, star-branched butyl rubber and halogenated star-branched butyl rubber, brominated butyl rubber, chlorinated butyl rubber, star-branched polyisobutylene rubber, star-branched brominated butyl (polyisobutylene/isoprene copolymer) rubber; poly(isobutylene-*co*-*p*-methylstyrene) and halogenated poly(isobutylene-*co*-*p*-methylstyrene), such as, for example, terpolymers of isobutylene derived units, *p*-methylstyrene derived units, and *p*-bromomethylstyrene derived units, and mixtures thereof.

A desirable embodiment of the secondary rubber component present is natural rubber. Natural rubbers are described in detail by *Subramaniam* in RUBBER TECHNOLOGY 179-208 (Maurice Morton, Chapman & Hall 1995). Desirable embodiments of the natural rubbers of the present invention are selected from Malaysian rubber such as SMR CV, SMR 5, SMR 10, SMR 20, and SMR 50 and mixtures thereof, wherein the natural rubbers have a Mooney viscosity at 100°C (ML 1+4) of from 30 to 120, more preferably from 40 to 65. The Mooney viscosity test referred to herein is in accordance with ASTM D-1646.

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Polybutadiene (BR) rubber is another desirable secondary rubber useful in the composition of the invention. The Mooney viscosity of the polybutadiene rubber as measured at 100°C (ML 1+4) may range from 35 to 70, from 40 to about 65 in another embodiment, and from 45 to 60 in yet another embodiment. Some commercial examples of these synthetic rubbers useful in the present invention are NATSYNTM (Goodyear Chemical Company), and BUDENE™ 1207 or BR 1207 (Goodyear Chemical Company). A desirable rubber is high cis-polybutadiene (cis-BR). By "cis-polybutadiene" or "high cis-polybutadiene", it is meant that 1,4-cis polybutadiene is used, wherein the amount of cis component is at least 95%. An example of high cis-polybutadiene commercial products used in the composition BUDENE™ 1207.

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Rubbers of ethylene and propylene derived units such as EPM and EPDM are also suitable as secondary rubbers. Examples of suitable comonomers in making EPDM are ethylidene norbornene, 1,4-hexadiene, dicyclopentadiene, as well as others. These rubbers are described in RUBBER TECHNOLOGY 260-283 (1995). A suitable ethylene-propylene rubber is commercially available as VISTALON™ (ExxonMobil Chemical Company, Houston TX).

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In another embodiment, the secondary rubber is a halogenated rubber as part of the terpolymer composition. The halogenated butyl rubber is brominated butyl rubber, and in another embodiment is chlorinated butyl rubber. General properties and processing of halogenated butyl rubbers is described in THE VANDERBILT RUBBER HANDBOOK 105-122 (Robert F. Ohm ed., R.T. Vanderbilt Co., Inc. 1990), and in RUBBER TECHNOLOGY 311-321 (1995). Butyl rubbers, halogenated butyl rubbers, and star-branched butyl rubbers are described by *Edward Kresge and H.C. Wang* in 8 KIRK-OTHMER ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY 934-955 (John Wiley & Sons, Inc. 4th ed. 1993).

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The secondary rubber component of the present invention includes, but is not limited to at least one or more of brominated butyl rubber, chlorinated butyl rubber, star-branched polyisobutylene rubber, star-branched brominated butyl (polyisobutylene/isoprene copolymer) rubber; halogenated poly(isobutylene-*co*-*p*-methylstyrene), such as, for example, terpolymers of isobutylene derived units, *p*-methylstyrene derived units, and *p*-bromomethylstyrene derived units (BrIBMS), and the like halomethylated aromatic interpolymers as in US5,162,445; US4,074,035; and US4,395,506; halogenated isoprene and halogenated isobutylene copolymers, polychloroprene, and the like, and mixtures of any of the above. Some embodiments of the halogenated rubber component are also described in US4,703,091 and US4,632,963.

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In one embodiment of the invention, a so called semi-crystalline copolymer ("SCC") is present as the secondary "rubber" component. Semi-crystalline copolymers are described in WO00/69966. Generally, the SCC is a copolymer of ethylene or propylene derived units and α -olefin derived units, the α -olefin having from 4 to 16 carbon atoms in one embodiment, and in another embodiment the SCC is a copolymer of ethylene derived units and α -olefin derived units, the α -olefin having from 4 to 10 carbon atoms, wherein the SCC has some degree of crystallinity. In a further embodiment, the SCC is a copolymer of 1-butene derived units and another α -olefin derived unit, the other α -olefin having from 5 to 16 carbon atoms, wherein the SCC also has some degree of crystallinity. The SCC can also be a copolymer of ethylene and styrene.

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The secondary rubber component of the elastomer composition may be present in a range from up to 90 phr in one embodiment, from up to 50 phr in another embodiment, from up to 40 phr in another embodiment, and from up to 30 phr in yet another embodiment. In yet another embodiment, the secondary rubber is present from at least 2 phr, and from at least 5 phr in another embodiment, and from at least 5 phr in yet another embodiment, and from at least 10 phr in yet

another embodiment. A desirable embodiment may include any combination of any upper phr limit and any lower phr limit. For example, the secondary rubber, either individually or as a blend of rubbers such as, for example NR and BR, may be present from 5 phr to 90 phr in one embodiment, and from 10 to 80 phr in another embodiment, and from 30 to 70 phr in yet another embodiment, and from 5 5
40 to 60 phr in yet another embodiment, and from 5 to 50 phr in yet another embodiment, and from 5 to 40 phr in yet another embodiment, and from 20 to 60 phr in yet another embodiment, and from 20 to 50 phr in yet another embodiment, the chosen embodiment depending upon the desired end use application of the 10 composition.

Thermoplastic

The composition of this invention may optionally include a thermoplastic resin. The thermoplastic engineering resins suitable for practice of the present 15 invention may be used singly or in combination and are resins containing nitrogen, oxygen, halogen, sulfur or other groups capable of interacting with an aromatic functional groups such as halogen or acidic groups. The resins are present in the nanocomposite from 30 to 90 wt% of the nanocomposite in one embodiment, and from 40 to 80 wt% in another embodiment, and from 50 to 70 wt% in yet another 20 embodiment. In yet another embodiment, the resin is present at a level of greater than 40 wt% of the nanocomposite, and greater than 60 wt% in another embodiment.

Suitable engineering resins include resins selected from the group 25 consisting of polyamides, polyimides, polycarbonates, polyesters, polysulfones, polylactones, polyacetals, acrylonitrile-butadiene-styrene resins (ABS), polyphenyleneoxide (PPO), polyphenylene sulfide (PPS), polystyrene, styrene-acrylonitrile resins (SAN), styrene maleic anhydride resins (SMA), aromatic polyketones (PEEK, PED, and PEKK) and mixtures thereof, and optionally, 30 polyolefins.

Suitable thermoplastic polyamides (nylons) comprise crystalline or resinous, high molecular weight solid polymers including copolymers and terpolymers having recurring amide units within the polymer chain. Polyamides may be prepared by polymerization of one or more epsilon lactams such as caprolactam, pyrrolidone, lauryllactam and aminoundecanoic lactam, or amino acid, or by condensation of dibasic acids and diamines. Both fiber-forming and molding grade nylons are suitable. Examples of such polyamides are polycaprolactam (nylon-6), polylauryllactam (nylon-12), polyhexamethyleneadipamide (nylon-6,6) polyhexamethyleneazelamide (nylon-6,9), polyhexamethylenesebacamide (nylon-6,10), polyhexamethyleneisophthalamide (nylon-6, IP) and the condensation product of 11-amino-undecanoic acid (nylon-11). Additional examples of satisfactory polyamides (especially those having a softening point below 275°C) are described in 16 ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY 1-105 (John Wiley & Sons 1968), CONCISE ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING 748-761 (John Wiley & Sons, 1990), and 10 ENCYCLOPEDIA OF POLYMER SCIENCE AND TECHNOLOGY 392-414 (John Wiley & Sons 1969). Commercially available thermoplastic polyamides may be advantageously used in the practice of this invention, with linear crystalline polyamides having a softening point or melting point between 160 and 260°C being preferred.

Suitable thermoplastic polyesters which may be employed include the polymer reaction products of one or a mixture of aliphatic or aromatic polycarboxylic acids esters of anhydrides and one or a mixture of diols. Examples of satisfactory polyesters include poly(trans-1,4-cyclohexylene), C₂₋₆ alkane dicarboxylates such as poly(trans-1,4-cyclohexylene succinate) and poly (trans-1,4-cyclohexylene adipate); poly (cis or trans-1,4-cyclohexanedimethylene) alkanedicarboxylates such as poly(cis-1,4-cyclohexane-di-methylene) oxlate and poly-(cis-1,4-cyclohexane-di-methylene) succinate, poly (C₂₋₄ alkylene

terephthalates) such as polyethyleneterephthalate and polytetramethylene-terephthalate, poly (C₂₋₄ alkylene isophthalates such as polyethyleneisophthalate and polytetramethylene-isophthalate and like materials. Preferred polyesters are derived from aromatic dicarboxylic acids such as naphthalenic or phthalic acids and C₂ to C₄ diols, such as polyethylene terephthalate and polybutylene terephthalate. Preferred polyesters will have a melting point in the range of 160°C to 260°C.

Poly(phenylene ether) (PPE) thermoplastic engineering resins which may be used in accordance with this invention are well known, commercially available materials produced by the oxidative coupling polymerization of alkyl substituted phenols. They are generally linear, amorphous polymers having a glass transition temperature in the range of 190°C to 235°C. These polymers, their method of preparation and blends with polystyrene are further described in US 3,383,435.

Other thermoplastic resins which may be used include the polycarbonate analogs of the polyesters described above such as segmented poly (ether co-phthalates); polycaprolactone polymers; styrene resins such as copolymers of styrene with less than 50 mol% of acrylonitrile (SAN) and resinous copolymers of styrene, acrylonitrile and butadiene (ABS); sulfone polymers such as polyphenyl sulfone; copolymers and homopolymers of ethylene and C₂ to C₈ α-olefins, in one embodiment a homopolymer of propylene derived units, and in another embodiment a random copolymer or block copolymer of ethylene derived units and propylene derived units, and like engineering resins as are known in the art.

The composition of the invention may also include one or more filler components such as calcium carbonate, clay, mica, silica and silicates, talc, titanium dioxide, and carbon black. In one embodiment, the filler is carbon black or modified carbon black. The preferred filler is semi-reinforcing grade carbon black present at a level of from 10 to 150 phr of the blend, more preferably from

30 to 120 phr. Useful grades of carbon black as described in RUBBER TECHNOLOGY 59-85 (1995) range from N110 to N990. More desirably, embodiments of the carbon black useful in, for example, tire treads are N229, N351, N339, N220, N234 and N110 provided in ASTM (D3037, D1510, and D3765). Embodiments of the carbon black useful in, for example, sidewalls in tires, are N330, N351, N550, N650, N660, and N762. Embodiments of the carbon black useful in, for example, innerliners for tires are N550, N650, N660, N762, and N990.

10 The composition of this invention may optionally include curative systems which are capable of curing the functionalized elastomeric copolymer component of the blend to provide vulcanizable compositions. Suitable curative systems for the elastomeric copolymer component of the present invention include organic peroxides, zinc oxide in combination with zinc stearate or stearic acid and, optionally, one or more of the following accelerators or vulcanizing agents: 15 Permalux (di-ortho-tolylguanidine salt of dicatechol borate), HVA-2 (m-phenylene bis maleimide), Zisnet (2, 4, 6- trimercapto- 5 triazine), ZDEDC (zinc diethyl dithiocarbamate) and other dithiocarbamates, Tetrone A (dipenta-methylene thiuram hexasulfide), Vultac-5 (alkylated phenol disulfide), SP1045 20 (phenol formaldehyde resin), SP1056 (brominated alkyl phenol formaldehyde resin), DPPD. (diphenyl phenylene diamine), salicyclic acid (o-hydroxy benzoic acid), wood rosin (abietic acid), and TMTDS (tetramethyl thiuram disulfide) in combination with sulfur. The composition may also be cured using ultraviolet light or electron irradiation.

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The compositions of the invention may also contain other conventional additives such as dyes, pigments, antioxidants, heat and light stabilizers, plasticizers, oils and other ingredients as known in the art.

Blending of the components may be carried out by combining the polymer components and the clay in the form of an intercalate in any suitable mixing device such as a Banbury™ mixer, Brabender™ mixer or preferably a mixer/extruder and mixing at temperatures in the range of 120° C up to 300° C under conditions of shear sufficient to allow the clay intercalate to exfoliate and become uniformly dispersed within the polymer to form the nanocomposite.

The composition of this invention may be extruded, compression molded, blow molded or injection molded into various shaped articles including fibers, films, industrial parts such as automotive parts, appliance housings, consumer products, packaging and the like. The resulting articles exhibit both high impact strength and low vapor permeability. In particular, the composition described herein is useful for air barriers such as bladders, and automotive (including truck, commercial and/or passenger) or aircraft innerliners and innertubes.

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Thus, one embodiment of the present invention includes a nanocomposite comprising one or more clays, an interpolymer, one or more exfoliating additives, wherein the exfoliating additive(s) is an amine having the structure $R^2R^3R^4N$, wherein R^2 , R^3 , and R^4 are C_1 to C_{20} alkyls or alkenes which may be the same or different. This composition is suitable for such articles as pneumatic tire components, especially treads, sidewalls, innerliners and innertubes. The composition is especially suitable for air barriers such as bladders, and innerliners for tires and innertubes. The composition may also comprise one or more polyfunctional curatives as described above.

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Another embodiment of the interpolymer suitable for compositions of the invention may be described as a polyisobutylene interpolymer comprising from 3 wt% to 15 wt% para-methylstyrene derived units and from 0.2 mol% to 1.5 mol% para-bromomethylstyrene derived units by weight of the interpolymer.

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In one embodiment of the composition or air barrier of the invention, the interpolymer is a copolymer of C₄ to C₇ isomonoolefin derived units, a para-methylstyrene derived units and a para-(halomethylstyrene) derived units, wherein the para-(halomethylstyrene) derived units are present from 0.4 to 1.5 mol% based on the total number of moles of monomer derived units incorporated into the interpolymer in one embodiment, and the para-methylstyrene is present from 3 wt% to 10 wt% by weight of the interpolymer.

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In one embodiment of the composition, the exfoliating amine can be described in that at least R² is a C₁₄ to C₂₀ alkyl or alkene. In yet another embodiment, the exfoliating agent is selected from N,N-dimethyl-octadecylamine, N,N-dioctadecyl-methylamine, dihydrogenated tallowalkyl-methylamine, amine-terminated polytetrahydrofuran and mixtures thereof.

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In yet another embodiment, the exfoliating agent is a thiosulfate compound or other compound selected from structures described by the formula Z--R⁷--Z', wherein R⁷ is one of a C₁ to C₁₅ alkyl, C₂ to C₁₅ alkenyl, and C₆ to C₁₂ cyclic aromatic moiety, substituted or unsubstituted; and Z and Z' are the same or different and are one of a thiosulfate group, mercapto group, aldehyde group, carboxylic acid group, peroxide group, alkenyl group, or other similar group that is capable of crosslinking, either intermolecularly or intramolecularly, one or more strands of a polymer having reactive groups such as unsaturation. In one embodiment, the thiosulfate compound is hexamethylene sodium thiosulfate.

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In yet another embodiment, the one or more polyfunctional curatives, when present, are selected from structures described by the formula Z--R⁷--Z', wherein R⁷ is one of a C₁ to C₁₅ alkyl, C₂ to C₁₅ alkenyl, and C₆ to C₁₂ cyclic aromatic moiety, substituted or unsubstituted; and Z and Z' are the same or different and are one of a thiosulfate group, mercapto group, aldehyde group, carboxylic acid group, peroxide group, alkenyl group, or other similar group that

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is capable of crosslinking, either intermolecularly or intramolecularly, one or more strands of a polymer having reactive groups such as unsaturation. Examples of such structures include hexamethylene bis(sodium thiosulfate) and hexamethylene bis(cinnamaldehyde), and mixtures thereof. Thus, these "polyfunctional curatives" may serve as the exfoliating additive alone, or may serve as a curative in addition to another exfoliating additive in one embodiment of the composition.

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In one embodiment, the exfoliating additive is present in the nanocomposite from 0.1 to 30 phr, and from 5 to 20 phr in another embodiment.

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In another embodiment of the composition, the alkylamine-exfoliated clay is a di-methyl tallowalkyl octyl ammonia methyl sulfate-exfoliated clay; and is present in the nanocomposite from 0.3 to 20 phr in yet another embodiment. In yet another embodiment, the alkylamine-exfoliated clay is a di-methyl di-hydrogenated tallow alkyl ammonia chloride-exfoliated clay.

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In another embodiment, the composition or air barrier may further comprising curing agents such as zinc, zinc stearate, stearic acid, sulfur, and mixtures thereof and other metals, metal oxides, and metal-carboxylic acid (fatty acid) complexes common in the rubber curing arts.

In yet another embodiment, the clay is pre-treated prior to blending with the interpolymer; the interpolymer, clay and exfoliating additive are added together (hence, not pre-treated) in yet another embodiment.

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The following examples are illustrative of the invention.

Test Methods & Examples

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Permeability Testing. All specimens were compression molded with slow cooling to provide defect free pads. A compression and curing press was used for

rubber samples. Typical thickness of a compression molded pad is around 15 mil. using an Arbor press, 2" diameter disks were then punched out from molded pads for permeability testing. These disks were conditioned in a vacuum oven at 60°C overnight prior to the measurement. The oxygen permeation measurements were 5 done using a Mocon OX-TRAN 2/61 permeability tester at 40°C under the principle of *R. A. Pasternak et. al.* in 8 JOURNAL OF POLYMER SCIENCE: PART A-2 467 (1970). Disks thus prepared were mounted on a template and sealed with a vacuum grease. 10 psi nitrogen was kept on one side of the disk, whereas the other side is 10 psi oxygen. Using the oxygen sensor on the nitrogen side, increase in 10 oxygen concentration on the nitrogen side with time could be monitored. The time required for oxygen to permeate through the disk, or for oxygen concentration on the nitrogen side to reach a constant value, is recorded and used to determine the oxygen permeability.

15 Mixing BIMS with Cloisite clays and amines was performed using a BrabenderTM mixer at 150°C and 60 RPM. Curatives were added subsequently in a mill. Cloisite clays were dried overnight prior to their usage in mixing. Compositions of these mixes are listed in Table 2. Tertiary amines were added in 0.5 and 1 mole equivalent of bromine, respectively. Rubber and tertiary amines 20 were added first for 6 minutes followed by Cloisite clay for another 5 minutes. All BIMS blends were cured to prepare pads for permeability measurement using a Mocon permeability tester. Permeability values are listed in Tables 2 through 5 for selected compositions 1A-8A, 1B-8B, 1C-8C, and 1D-4D. The data show that the addition of the tertiary amines and polyfunctional curatives improves the air 25 impermeability of the BIMS interpolymer. In Table 4, the addition of a pre-treated clay along with a tertiary amine is shown to further improve the air impermeability of the BIMS interpolymer samples 3C and 7C. In Table 5, the addition of the treated clay and amine is shown to improve the air permeability of a BIMS interpolymer having a bromine level of 1.2 mol%.

The oxygen permeability (cc·mil/(m²·day·mmHg)) of the nanocomposites of the present invention, at 40°C, range from less than 20 cc·mil/(m²·day·mmHg) in one embodiment, and less than 18 cc·mil/(m²·day·mmHg) in another embodiment, and less than 15 cc·mil/(m²·day·mmHg) in yet another embodiment, 5 and desirably less than 13 cc·mil/(m²·day·mmHg) in yet another embodiment, and less than 10 cc·mil/(m²·day·mmHg) in yet another embodiment.

Embodiments of the final nanocomposite of the present invention are useful as air barriers, such as used in producing innerliners for motor vehicles. In 10 particular, the nanocomposites are useful in innerliners and innertubes for articles such as truck tires, bus tires, passenger automobile, motorcycle tires, off the road tires, and the like. The improved heat aging resistance of the present innerliner composition makes it particularly suited for use in truck tires to increase the retreading capability of the tire.

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While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to many different variations not illustrated herein. For these 20 reasons, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

Table 1. Material Description

Designation	Description	Material
BIMS 8-94	BIMS 89-4 rubber, 45 ML*, 0.75 mol % Br, 5 wt % PMS	EXXPRO 89-4, ExxonMobil Chemical
BIMS 3035	BIMS 3035 rubber, 45 ML*, 0.48 mol % Br, 5 wt % PMS	EXXPRO Elastomers 3035, ExxonMobil Chemical
BIMS 3745	BIMS 3745 rubber, 45 ML*, 1.2 mol % Br, 7.5 wt % PMS	EXXPRO Elastomers 3745, ExxonMobil Chemical
DM16D	Tertiary amine, hexadecyl-dimethylamine	Armeen DM16D, Akzo Nobel Chemical
M2HT	Tertiary amine, dihydrogenated tallowalkyl-methylamine**	Armeen M2HT, Akzo Nobel Chemical
6A	Montmorillonite clay treated with di-methyl di-hydrogenated tallow alkyl ammonia chloride	Cloisite 6A, Southern Clay
Na	Montmorillonite clay with Na counter ions	Cloisite Na, Southern Clay
HTS	Hexamethylene bisthiosulfate disodium salt	Flexsys Duralink HTS
Acetylene Black	Carbon Black	e.g., Harwick Standard; R.T. Vanderbilt; Degussa-Huls.
THF-N	Amine terminated polytetrahydrofuran	Aldrich Chemical

*: ML is Mooney viscosity (1+8) measured at 125°C and ~1 s⁻¹.

**: hydrogenated tallow contains saturated 3.5% C14, 0.5% C15, 31% C16, 1% C17, 61% C18 and unsaturated 3% C18 (2/3 of the alkyl group is C18)

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Table 2. BIMS Clays Blends with DM16D/M2HT and Na (Untreated Clay)

Component (phr)	1A	2A	3A	4A	5A	6A	7A	8A
BIMS 8-94	200	200	200	200	180	180	180	180
Na (Clay)	10	10	10	10	18	18	18	18
DM16D (t-amine)	3.6	7.2	0	0	3.2	6.4	0	0
M2HT (t-amine)	0	0	7	14	0	0	6.3	12.6
ZnO	2	2	2	2	1.8	1.8	1.8	1.8
Zn Stearate	2	2	2	2	1.8	1.8	1.8	1.8
Stearic Acid	4	4	4	4	3.6	3.6	3.6	3.6
Permeability (cc·mil/(m ² ·day·mmHg))	-	-	25.1	26.9	-	-	22.3	25.4

Table 3. BIMS Clay Blends with HTS/THF-N

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Component (phr)	1B	2B	3B	4B	5B	6B	7B	8B
BIMS 3035	100	100	100	100	100	100	100	100
THF-N (amine)	0	0	0	0	0	0	1	1
6A (clay)	0	0	9	0	9	0	0	0
Na (clay)	0	0	0	9	0	9	9	9
Carbon Black	30	30	30	30	30	30	30	30
Zinc Oxide	2	0	2	2	0	0	2	0
Zinc Octoate	0	2	0	0	2	2	0	2
HTS (thiosulfate)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Permeability (cc·mil/(m ² ·day·mmHg))	19.1	19.9	18.7	16.9	19.3	17.0	17.1	16.8

Table 4. BIMS Clays Blends with DM16D/M2HT and 6A (Treated Clay)

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Component (phr)	1C	2C	3C	4C	5C	6C	7C	8C
BIMS 8-94	200	200	200	200	180	180	180	180
6A (clay)	10	10	10	10	18	18	18	18
DM16D (amine)	3.6	7.2	0	0	3.2	6.4	0	0
M2HT (amine)	0	0	7	14	0	0	6.3	12.6
ZnO	2	2	2	2	1.8	1.8	1.8	1.8
Zn Stearate	2	2	2	2	1.8	1.8	1.8	1.8
Stearic Acid	4	4	4	4	3.6	3.6	3.6	3.6
Permeability (cc·mil/(m ² ·day·mmHg))	23.7	-	17.3	-	-	-	15.7	-

Table 5. BIMS/CB Compounds Containing Clays and DM16D/M2HT

Component (phr)	1D	2D	3D	4D
BIMS 3745	100	100	100	100
N660 (carbon black)	60	60	60	60
6A (clay)	0	3	3	3
DM16D (amine)	0	0	1.48	0
M2HT (amine)	0	0	0	0.96
ZnO	1	1	1	1
MBTS	1.25	1.25	1.25	1.25
S	0.5	0.5	0.5	0.5
Stearic Acid	1	1	1	1
Permeability (cc·mil/(m ² ·day·mmHg))	15.85	15.38	13.68	12.92

CLAIMS:

1. A nanocomposite comprising a nano-clay dispersed in an elastomeric matrix interpolymer, and one or more exfoliating additives; wherein the one or more exfoliating additives is

- (1) an amine having the structure $R^2R^3R^4N$, wherein R^2 , R^3 , and R^4 are C_1 to C_{20} alkyls or alkenes which are the same or different,
- (2) an ammonium corresponding thereto,
- (3) a polyfunctional amine or ammonium, or
- (4) a structure described by the formula $Z--R^7--Z'$, wherein R^7 is one of a C_1 to C_{15} alkyl, C_2 to C_{15} alkenyl, and C_6 to C_{12} cyclic aromatic moiety, substituted or unsubstituted; and Z and Z' are the same or different and are one of a thiosulfate group, mercapto group, aldehyde group, carboxylic acid group, peroxide group, alkenyl group, or other similar group that is capable of crosslinking, either intermolecularly or intramolecularly, one or more strands of a polymer having reactive groups; and

wherein the elastomeric matrix interpolymer is a) an interpolymer of C_4 to C_7 isomonoolefin derived units, a para-methylstyrene derived units and a para-(halomethylstyrene) derived units or b) a halogenated elastomer comprising C_4 to C_7 isomonoolefin derived units, multiolefin derived units, and halogenated multiolefin derived units.

2. The nanocomposite of claim 1, wherein the interpolymer is a copolymer of C_4 to C_7 isomonoolefin derived units, a para-methylstyrene derived units and a para-(halomethylstyrene) derived units.

3. The nanocomposite of claim 1 or 2, wherein the para-(halomethylstyrene) derived units are present from 0.4 to 1.5 mol% in the interpolymer.

4. The nanocomposite of claim 1, wherein at least one of R², R³, and R⁴ is a C₁₄ to C₂₀ alkyl or alkene.
5. The nanocomposite of claim 4, wherein the one or more exfoliating additives is N,N-dimethyl-octadecylamine, N,N-dioctadecyl-methylamine, dihydrogenated tallowalkyl-methylamine, amine-terminated polytetrahydrofuran or a mixture thereof.
6. The nanocomposite of claim 1, wherein the one or more exfoliating additives is (4) the structure described by the formula Z--R⁷--Z', wherein R⁷ is one of C₁ to C₁₅ alkyl, C₂ to C₁₅ alkenyl, and C₆ to C₁₂ cyclic aromatic moiety, substituted or unsubstituted; and Z and Z' are the same or different and are one of the thiosulfate group, mercapto group, aldehyde group, carboxylic acid group, peroxide group, alkenyl group, or other similar group that is capable of crosslinking, either intermolecularly or intramolecularly, one or more strands of the polymer having reactive groups.
7. The nanocomposite of claim 6, wherein the exfoliating additive is a thiosulfate compound.
8. The nanocomposite of claim 1, also comprising carbon black.
9. The nanocomposite of claim 1, also comprising one or more polyfunctional curatives.
10. The nanocomposite of claim 1, wherein the exfoliating additive is present in the nanocomposite from 0.1 to 20 phr.
11. The nanocomposite of claim 1, wherein the nano-clay is a di-methyl tallowalkyl octyl ammonium methyl sulfate-exfoliated clay.

12. The nanocomposite of claim 1, wherein the nano-clay is present in the nanocomposite from 0.2 to 15 phr.
13. The nanocomposite of claim 1, wherein the nano-clay is a di-methyl di-hydrogenated tallowalkyl ammonium chloride-exfoliated clay.
14. The nanocomposite of claim 1, further comprising curing agents.
15. The nanocomposite of claim 14, wherein the curing agents comprise zinc, zinc stearate, stearic acid, sulfur, or a mixture thereof.
16. The nanocomposite of claim 1, wherein the nano-clay is pre-treated.
17. The nanocomposite of claim 1, also comprising a secondary rubber which is a natural rubber, polybutadiene rubber, nitrile rubber, silicon rubber, polyisoprene rubber, poly(styrene-*co*-butadiene) rubber, poly(isoprene-*co*-butadiene) rubber, styrene-isoprene-butadiene rubber, ethylene-propylene rubber, brominated butyl rubber, chlorinated butyl rubber, halogenated isoprene, halogenated isobutylene copolymers, polychloroprene, star-branched polyisobutylene rubber, star-branched brominated butyl rubber, poly(isobutylene-*co*-isoprene) rubber, halogenated poly(isobutylene-*co*-*p*-methylstyrene) or a mixture thereof.
18. An innerliner comprising the nanocomposite of claim 1.
19. An innertube comprising the nanocomposite of claim 1.
20. A nanocomposite comprising at least one nano-clay uniformly dispersed in an elastomeric matrix comprising at least one isobutylene interpolymer comprising from 3 wt% to 15 wt% para-methylstyrene derived units and from 0.2 mol% to 1.5 mol% para-

bromomethylstyrene derived units by weight of the interpolymer; one or more exfoliating additives; wherein the one or more exfoliating additive is an amine having the structure $R^2R^3R^4N$, wherein R^2 , R^3 , and R^4 are C_1 to C_{30} alkyls or alkenyls which are the same or different.

21. The nanocomposite of claim 20, wherein the para-(halomethylstyrene) derived units are present from 0.4 to 1.5 mol% in the interpolymer.
22. The nanocomposite of claim 20, wherein at least one of R^2 , R^3 , and R^4 is a C_{14} to C_{20} alkyl or alkene.
23. The nanocomposite of claim 20, wherein the exfoliating additive is N,N-dimethyl-octadecylamine, N,N-dioctadecyl-methylamine, dihydrogenated tallowalkyl-methylamine, amine-terminated polytetrahydrofuran or a mixture thereof.
24. The nanocomposite of claim 20, wherein the exfoliating additive is an amine having the structure $R^2R^3R^4N$, wherein R^2 , R^3 , and R^4 are C_1 to C_{20} alkyls or alkenes which may be the same or different.
25. The nanocomposite of claim 20, wherein the exfoliating additive further comprises a composition having a structure described by the formula $Z--R^7--Z'$, wherein R^7 is one of a C_1 to C_{15} alkyl, C_2 to C_{15} alkenyl, and C_6 to C_{12} cyclic aromatic moiety, substituted or unsubstituted; and Z and Z' are the same or different and are one of a thiosulfate group, mercapto group, aldehyde group, carboxylic acid group, peroxide group, alkenyl group, or other similar group that is capable of crosslinking, either intermolecularly or intramolecularly, one or more strands of a polymer having reactive groups.

26. The nanocomposite of claim 20, wherein the exfoliating additive further comprises a thiosulfate compound.
27. The nanocomposite of claim 20, also comprising carbon black.
28. The nanocomposite of claim 20, also comprising one or more polyfunctional curatives.
29. The nanocomposite of claim 20, wherein the exfoliating additive is present in the nanocomposite from 0.1 to 20 phr.
30. The nanocomposite of claim 20, wherein the nano-clay is a di-methyl tallowalkyl octyl ammonium methyl sulfate-exfoliated clay.
31. The nanocomposite of claim 20, wherein the nano-clay is present in the nanocomposite from 0.2 to 15 phr.
32. The nanocomposite of claim 20, wherein the nano-clay is a di-methyl di-hydrogenated tallowalkyl ammonium chloride-exfoliated clay.
33. The nanocomposite of claim 20, further comprising curing agents.
34. The nanocomposite of claim 20, wherein the curing agents comprise zinc, zinc stearate, stearic acid, sulfur, or a mixture thereof.
35. The nanocomposite of claim 20, also comprising a secondary rubber which is natural rubber, polybutadiene rubber, nitrile rubber, silicon rubber, polyisoprene rubber, poly(styrene-*co*-butadiene) rubber, poly(isoprene-*co*-butadiene) rubber, styrene-isoprene-butadiene rubber, ethylene-propylene rubber, brominated butyl rubber, chlorinated butyl rubber, halogenated

isoprene, halogenated isobutylene copolymers, polychloroprene, star-branched polyisobutylene rubber, star-branched brominated butyl rubber, poly(isobutylene-*co*-isoprene) rubber, halogenated poly(isobutylene-*co*-*p*-methylstyrene) or a mixture thereof.

36. An innerliner comprising the nanocomposite of claim 20.

37. A bladder comprising the nanocomposite of claim 20.

38. An innertube comprising the nanocomposite of claim 20.

39. A nanocomposite comprising at least one nano-clay uniformly dispersed in a butyl rubber comprising C₄ to C₇ isoolefin derived units, multiolefin derived units, and halogenated multiolefin derived units, and one or more exfoliating additives; wherein the exfoliating additive is

(1) an amine having the structure R²R³R⁴N, wherein R², R³, and R⁴ are C₁ to C₂₀ alkyls or alkenes which are the same or different,

(2) a corresponding ammonium,

(3) a polyfunctional amine or ammonium, or

(4) a structure described by the formula Z--R⁷--Z', wherein R⁷ is one of a C₁ to C₁₅ alkyl, C₂ to C₁₅ alkenyl, and C₆ to C₁₂ cyclic aromatic moiety, substituted or unsubstituted; and Z and Z' are the same or different and are one of a thiosulfate group, mercapto group, aldehyde group, carboxylic acid group, peroxide group, alkenyl group, or other similar group that is capable of crosslinking, either intermolecularly or intramolecularly, one or more strands of a polymer having reactive groups.

40. The nanocomposite of claim 39, wherein the halogenated multiolefin units are primary allylic halogenated units present to at least 20 mol%.

41. The nanocomposite of claim 39, wherein at least one of R², R³, and R⁴ is a C₁₄ to C₂₀ alkyl or alkene.
42. The nanocomposite of claim 39, wherein the exfoliating additive is N,N-dimethyl-octadecylamine, N,N-dioctadecyl-methylamine, dihydrogenated tallowalkyl-methylamine, amine-terminated polytetrahydrofuran or a mixture thereof.
43. The nanocomposite of claim 39, wherein the exfoliating additive is a structure described by the formula Z--R⁷--Z', wherein R⁷ is one of a C₁ to C₁₅ alkyl, C₂ to C₁₅ alkenyl, and C₆ to C₁₂ cyclic aromatic moiety, substituted or unsubstituted; and Z and Z' are the same or different and are one of a thiosulfate group, mercapto group, aldehyde group, carboxylic acid group, peroxide group, alkenyl group, or other similar group that is capable of crosslinking, either intermolecularly or intramolecularly, one or more strands of a polymer having reactive groups.
44. The nanocomposite of claim 39, wherein the exfoliating additive is a thiosulfate compound.
45. The nanocomposite of claim 39, also comprising carbon black.
46. The nanocomposite of claim 39, also comprising one or more polyfunctional curatives.
47. The nanocomposite of claim 39, wherein the exfoliating additive is present in the nanocomposite from 0.1 to 20 phr.
48. The nanocomposite of claim 39, wherein the nano-clay is a di-methyl tallowalkyl octyl ammonium methyl sulfate-exfoliated clay.

49. The nanocomposite of claim 39, wherein the nano-clay is present in the nanocomposite from 0.2 to 15 phr.
50. The nanocomposite of claim 39, wherein the nano-clay is a di-methyl di-hydrogenated tallowalkyl ammonium chloride-exfoliated clay.
51. The nanocomposite of claim 39, further comprising curing agents.
52. The nanocomposite of claim 51, wherein the curing agents comprise zinc, zinc stearate, stearic acid, sulfur, or a mixture thereof.
53. The nanocomposite of claim 39, wherein the nano-clay is pre-treated.
54. The nanocomposite of claim 39, also comprising a secondary rubber which is natural rubber, polybutadiene rubber, nitrile rubber, silicon rubber, polyisoprene rubber, poly(styrene-*co*-butadiene) rubber, poly(isoprene-*co*-butadiene) rubber, styrene-isoprene-butadiene rubber, ethylene-propylene rubber, brominated butyl rubber, chlorinated butyl rubber, halogenated isoprene, halogenated isobutylene copolymers, polychloroprene, star-branched polyisobutylene rubber, star-branched brominated butyl rubber, poly(isobutylene-*co*-isoprene) rubber, halogenated poly(isobutylene-*co*-*p*-methylstyrene) or a mixture thereof.
55. A tire innerliner comprising the nanocomposite of claim 39.
56. An innertube comprising the nanocomposite of claim 39.