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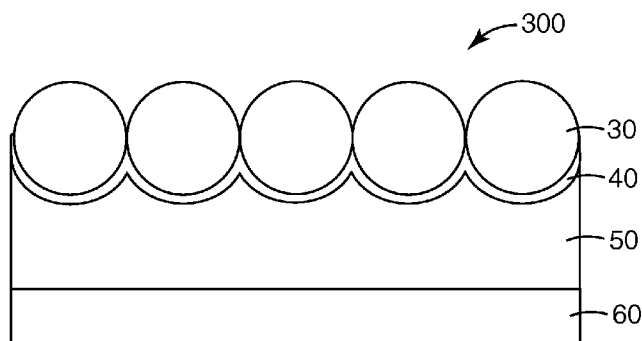


Fig. 3

(57) Abstract: Retroreflective vulcanized rubber articles with retroreflective sheeting bonded to it are provided. The retroreflective sheeting contains a plurality of retroreflective elements at least partially embedded in a polyurethane binder layer. The polyurethane binder layer contains the reaction product of at least one diisocyanate, at least one polyisocyanate, at least one polyol, at least one unsaturated polyol, and at least one chain extension agent. Also, methods for preparing retroreflective vulcanized rubber articles are provided.

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RETROREFLECTIVE TIRE

Field of the Disclosure

This disclosure relates to retroreflective vulcanized rubber articles such as retroreflective tires. Also disclosed are methods for making such articles using retroreflective sheeting.

Background

Retroreflectivity is a phenomenon that has been successfully used to prepare safety related articles. Retroreflection may be defined as a phenomenon in which a large portion of luminous radiation is returned in the direction from which it originates. This may be achieved through the use of spherical retroreflectors, which may be glass beads or microspheres that are at least partially coated with a reflective material, directly or via an intermediate layer.

Among the articles that can benefit from the use of retroreflectivity are rubber articles such as tires. Bicycle and motorcycle tires are a particular example since visibility at night is a particular safety issue for cyclists. Frequently cycles come with attached reflectors on the frame and/or the tire rims, but often the tires themselves are not reflective. If the tires are reflective they are generally made retroreflective by the attachment of a reflector or the compounding of retroreflective elements with the tire when it is manufactured. However, often when a reflector is attached to a tire, the attached reflectors may not provide good visibility due to the limited area which is covered and the ease with which the attached reflectors can be damaged or fall off. An issue with compounding retroreflective beads with the tire is that such reflectors generally provide poor brightness.

Summary

Methods to incorporate retroreflectivity into rubber articles, such as tires, such that the retroreflectivity is retained in use is desirable. Retroreflective vulcanized rubber articles with retroreflective sheeting bonded to it are provided. In some embodiments the vulcanized rubber article comprises a vulcanized rubber portion; and a retroreflective sheeting element comprising a polyurethane binder layer with first and second surfaces;

and, a plurality of retroreflective elements at least partially embedded in the first surface; wherein the second surface of the polyurethane binder layer is directly bonded to the vulcanized rubber portion. The retroreflective elements may be, for example, metal-coated microspheres. The polyurethane binder comprises the reaction product of at least one diisocyanate, at least one polyisocyanate, at least one polyol, at least one unsaturated polyol, and at least one chain extension agent. The polyurethane binder may also comprise a polyol with a functionality greater than 2. In some embodiments the polyurethane binder also contains a silane coupling agent.

Methods for preparing retroreflective vulcanized rubber articles are also provided. In some embodiments, the method of making a vulcanized rubber article comprises providing a retroreflective sheeting element comprising a polyurethane binder layer with first and second surfaces having unsaturated sites for co-vulcanization, and a plurality of retroreflective elements partially embedded in the first surface; contacting the second surface of the polyurethane binder layer with unvulcanized rubber material; and vulcanizing the unvulcanized rubber material under heat and pressure such that the second surface of the binder layer of the retroreflective sheeting element is bonded to the vulcanized rubber material. In some embodiments, contacting the second surface of the polyurethane binder layer with unvulcanized rubber material comprises placing the retroreflective sheeting and the unvulcanized rubber into a mold and applying heat and pressure. The polyurethane binder comprises the reaction product of at least one diisocyanate, at least one polyisocyanate, at least one polyol, at least one unsaturated polyol, and at least one chain extension agent. In some embodiments, the polyurethane binder is the reaction product of a two part reaction mixture wherein the first part comprises a polyurethane prepolymer comprising at least one diisocyanate, at least one polyisocyanate, at least one polyol, at least one unsaturated polyol and the second part comprises at least one chain extension agent.

Brief Description of the Drawings

Figure 1 shows a schematic cross sectional view of a segment of co-vulcanizable retroreflective sheeting as described in the present disclosure.

Figure 2 shows a schematic cross sectional view of a segment of co-vulcanizable retroreflective sheeting as described in the present disclosure.

Figure 3 shows a schematic cross sectional view of a segment of a vulcanized rubber article as described in the present disclosure.

Detailed Description

5 Retroreflective vulcanized rubber articles with retroreflective sheeting bonded to it are provided. The articles are prepared from retroreflective sheeting which contains retroreflective elements and a polyurethane binder. The polyurethane binder is co-vulcanized with unvulcanized rubber to form the rubber article. In some embodiments the rubber article is a tire, such as a bicycle tire.

10 The retroreflective sheeting comprises a plurality of retroreflective elements at least partially embedded in a polyurethane binder. The polyurethane binder preferably is the reaction product of at least one diisocyanate, at least one polyisocyanate, at least one polyol, at least one unsaturated polyol, and at least one chain extension agent.

15 The diisocyanate component of the polyurethane binder may be any aliphatic, cycloaliphatic, aromatic or heterocyclic diisocyanate, or any combination of such diisocyanates. Particularly suitable diisocyanates correspond to the formula:



in which Q represents:

20 an aliphatic hydrocarbon radical containing from 2 to 100 carbon atoms and zero to 50 heteroatoms;

a cycloaliphatic hydrocarbon radical containing from 4 to 100 carbon atoms and zero to 50 heteroatoms;

25 an aromatic hydrocarbon radical or heterocyclic aromatic radical containing from 5 to 15 carbon atoms and zero to 10 heteroatoms; or an araliphatic hydrocarbon radical containing from 8 to 100 carbon atoms and zero to 50 heteroatoms.

The heteroatoms that may be present in Q include non-peroxidic oxygen, sulfur, non-amino nitrogen, halogen, silicon, and non-phosphino phosphorous.

Illustrative examples of suitable diisocyanates include ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, trimethyl hexamethylene

diisocyanate, 1,12-dodecane diisocyanate, cyclobutane-1,3-diisocyanate, cyclohexane-1,3- and -1,4-diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanotomethylcyclohexane (isophorone diisocyanate, IDPI), 2,4- and 2,6-hexahydrotolylene diisocyanate, perhydro-2,4'- and -4,4'-diphenylmethane diisocyanate (H_{12} MDI), hexahydro-1,3- and -1,4-phenylene diisocyanate, 1,3- and -1,4-phenylene diisocyanate, 2,4- and 2,6-tolylene diisocyanate, diphenylmethane-2,4'- and -4,4'-diisocyanate, mixtures of 2,2,4- and 2,4,4-trimethyl hexamethylene diisocyanate (TMDI), naphthylene-1,5-diisocyanate, including mixtures of these isomers, as well as oligomers thereof, and any combination of the above diisocyanates.

Diisocyanates that are commercially available and which impart good processability to the urethane prepolymer are preferred. Illustrative examples of such diisocyanates include hexamethylene diisocyanate, methylene-bis-(4-cyclohexylisocyanate), isophorone diisocyanate, naphthalene 1,5-diisocyanate, toluene diisocyanate, isomers of diphenylmethane diisocyanate, or a mixture thereof. Isophorone diisocyanate, such as DESMODUR I commercially available from Bayer MaterialScience, Leverkusen, Germany, is particularly useful.

The polyisocyanate component of the polyurethane binder is similar to the diisocyanate component described above but is generally a higher molecular weight analog prepared by chain extension of diisocyanates. These higher molecular weight analogs may be aliphatic, cycloaliphatic, aromatic or heterocyclic diisocyanate, or any combination thereof. In addition the functionality of the polyisocyanates may be greater than 2. An example of a useful polyisocyanate is the commercially available DESMODUR VL from Bayer MaterialScience, Leverkusen, Germany which is an aromatic polyisocyanate based on diphenylmethane diisocyanate.

Generally the amount of polyisocyanate is 5-30 weight percent of the amount of diisocyanate. In some embodiments, the amount of polyisocyanate is 10-20 percent by weight of the amount of diisocyanate.

The polyol component of the polyurethane binder may be in a liquid form, or may be an oligomeric difunctional alcohol. The polyol preferably has a number average molecular weight (M_n) ranging from about 90 to about 5,000 or even about 90 to about 1,000 g/mole. Illustrative examples of suitable polyols include the CARBOWAX 400,

600, 800 and 1000 series of poly(ethylene oxide) compounds (commercially available from Dow Chemical, Midland, MI), caprolactone polyols such as the TONE 200, 201, 210, 230, 240 and 260 series of polyols (commercially available from Dow Chemical), poly(tetramethylene oxide) polyols such as the Poly THF 250, 650, 1000 and 2000 series of polyols (commercially available from BASF Corp., Parsippany, NJ), polypropylene oxide polyols, polycarbonate polyols, such as KM-10-1667 and KM-10-1733 polycarbonate diols (commercially available from Stahl USA, Peabody, Mass.) and the DESMOPHEN series of polycarbonate diols such as DESMOPHEN C 1200 and DESMOPHEN X 2501 polycarbonate diols (commercially available from Bayer MaterialScience, Leverkusen, Germany), polyurethane polyols, such as K-flex UD-320-100 polyurethane diols (commercially available from King Industries, Norwalk, CN), aromatic polyether polyols, such as SYNFAC 8024 polyols (commercially available from Milliken Chemical, Spartanburg, SC), and random copolymers of poly(tetramethylene oxide)polycarbonate, such as the Poly THF CD series of polyols (commercially available from BASF Corporation, Mount Olive, NJ). Polyester polyols include the FOMREZ family (commercially available from Chemtura Corporation, Middlebury, CT), such as FOMREZ 11-112, 22-55, 33-56, 44-58, 55-112 polyols or the RUCOFLEX family (commercially available from RUCO Polymer Corporation, Hicksville, N.Y.) such as RUCOFLEX S-101, S-102, S-105, S-107, S-1014, S-1021, S-1028 and S-1034 diols. Polycaprolactone polyols, polycarbonate polyols, polyurethane diols and polyester polyols are generally preferred for weatherability reasons.

Other polyols suitable for use in the invention include the hydroxyalkyl ethers obtained by the addition of optionally substituted alkylene oxides, such as ethylene oxide, propylene oxide, butylene oxide and styrene oxide, onto the abovementioned polyols.

Preferred examples of such hydroxyalkyl ether polyols include diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol, dibutylene glycol, 1,4-bis-(2-hydroxyethoxy)cyclohexane and 1,4-bis-(2-hydroxyethoxy-methyl)-cyclohexane, 1,4-bis-(2-hydroxyethoxy)-benzene. These materials have relatively low molecular weights and help incorporate rigidity into the urethane prepolymer backbone.

In addition to the above, in some embodiments one or more polyols with a functionality greater than 2 such as trifunctional or greater-functional polyols may be

added to the polyurethane binder at a level which will not hamper the thermoformability of the binder. Examples of trifunctional or greater-functional polyols include glycerol, trimethylol propane, trimethylol ethane, 1,2,6-hexane triol, 1,2,4-butanetriol, pentaerythritol, mannitol, sorbitol, formitol and mixtures thereof. In addition, polymeric multifunctional polyols may be used. Examples of such polyols include, for example, some of the DESMOPHEN polyols such as DESMOPHEN 670 and DESMOPHEN 800 commercially available from Bayer MaterialScience, Leverkusen, Germany.

The unsaturated polyol component of the polyurethane binder may be any aliphatic, cycloaliphatic, aromatic or heterocyclic polyol, or any combination of such polyols that contain unsaturated groups. Particularly suitable polyols correspond to the formula:



in which n is 2 or greater and Z represents an n valent, hydrocarbon-based, radical which contains unsaturated groups along or pendant from the hydrocarbon chain. The hydrocarbon-based group may or may not contain heteroatoms.

A variety of unsaturated polyol materials are commercially available including, for example, hydroxy-terminated polybutadiene materials, such as the POLY BD series of polyols (commercially available from ATOFINA Chemical, Philadelphia, PA), including POLY BD R-45HTLO, POLY BD R-20LM, POLY BD 600 and POLY BD 605. Another class of commercially available unsaturated polyols are the HTBNs (hydroxy-terminated poly(butadiene-co-acrylonitrile)) liquid rubbers.

Generally, the amount of unsaturated polyol is 1-99 weight percent of the total polyol content of the polyurethane binder composition, more typically 40-80 weight percent of the total polyol content.

The chain extension agent component of the polyurethane binder is typically a diol. The diols are typically low molecular weight, short chain diols well known in the polyurethane art. In some embodiments the chain transfer agent has a number average molecular weight of 120 or less. Chain extension agents are generally incorporated into polyurethane backbones, to improve ductility or strength characteristics. These diols may be aliphatic, aromatic, cycloaliphatic or combinations thereof. Among the chain extension agents useful in the present disclosure are, for example, ethylene glycol, 1,4-butanediol,

diethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,6-hexanediol, hydroquinone bis(2-hydroxyethyl) ether (HQEE), bisphenol A, bisphenol F, 2,2,4-trimethyl-1,3-pentanediol, dipropylene glycol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, 1,4-cyclohexanedimethanol, cyclohexanediol, and the like.

5 The polyurethane binder may additionally comprise other materials typically used in the generation of preparation of polyurethane polymers. Among these are catalysts, fillers, leveling agents, defoamers, colorants, antioxidants, UV light stabilizers and the like.

10 Catalysts for the reaction of polyisocyanates and active hydrogen-containing compounds are well-known in the art; see, for example, U.S. Pat. No. 4,495,061 (Mayer et al.). Preferred catalysts include organometallic compounds and amines. The organometallic compounds may be organotin compounds such as dimethyltin dilaurate, dibutyltin dilaurate, dibutyltin dimercaptide, dimethyltin dithioglycolate, and dioctyltin dithioglycolate. The amine catalysts preferably are tertiary amines such as triethylene
15 diamine, dimorpholinodiethyl ether, and tris(dimethylamino ethyl)phenol. Generally, the catalyst is present in the reaction mixture at 50 ppm (parts per million by weight of the total composition) to 50,000 ppm, or 100 ppm to 2,000 ppm, or even 200 to 1,000 ppm.

20 Useful fillers that may be used in the polyurethane binder composition include, for example, carbon black, metal oxides such as silica, alumina, titanium oxide and the like. Any suitable filler may be used as long as it doesn't interfere with the preparation or use of the polyurethane binder composition.

25 In some embodiments, a silane coupling agent may be used in the polyurethane binder composition. Silane coupling agents are reagents well known in the polyurethane art. Typically the silane coupling agents are bifunctional having a silane or substituted silane group on one end and a reactive group on the other end. Examples of silane groups include silane, alkyl silanes and alkoxy silanes. Reactive groups suitable for use with polyurethane systems include any group which may react with an isocyanate or a polyol. Such groups include, for example, isocyanate groups, primary or secondary amine groups, hydroxyl groups, epoxy groups, thiol groups, acetic acid groups and the like. Examples of
30 particularly suitable silane coupling agents include, for example, such compounds as KH-560 a commercially available coupling agent of (3 glycidyloxypropyl) trimethoxy silane or Z 6020, Z 6040, KH-550, commercially available from Dow Corning, Midland, MI. If

used, the silane coupling agent is generally present in the amount of 0.1 to 7 weight percent based on the total weight of the polyurethane binder composition. In some embodiments, the amount of silane coupling agent is 1-3 weight percent.

5 The retroreflective sheeting comprises a plurality of retroreflective elements at least partially embedded in the polyurethane binder. In some embodiments, the retroreflective elements are retroreflective beads. Among the retroreflective beads useful for this application are microspheres that, generally, are substantially spherical in shape in order to provide the most uniform and efficient retroreflection. The microspheres preferably also are substantially transparent so as to minimize absorption of light so that a large percentage of incident light is retroreflected. The term "transparent" is used herein to mean capable of transmitting light. The microspheres often are substantially colorless but may be tinted or colored in some other fashion. The microspheres may be made from glass, a non-vitreous ceramic composition, or a synthetic resin. In general, glass microspheres are preferred because they tend to be less expensive, harder, and more durable than microspheres made from synthetic resins.

10 The microspheres may have any suitable size. Typically, the microspheres have an average diameter in the range of about 10 to 200 micrometers, or about 25 to 80 micrometers. Microspheres used in some embodiments typically have a refractive index of about 1.91, although values in the range of about 1.5 to 2.5, or any other suitable values, may be useful as well, depending on the type of sheeting desired.

20 The microspheres may have a reflective metal layer disposed beneath the embedded portions of the microspheres. Generally, the reflective layer is disposed on the embedded or rear portions of the microspheres. The reflective layer may be disposed directly on the microspheres or it can be disposed on the microspheres via an intermediate layer. The term "reflective layer" is used herein to mean any suitable layer capable of reflecting light, and preferably it is capable of specularly reflecting light. In one exemplary embodiment, the reflective layer may be a layer comprising elemental metal. The metal may be a continuous coating produced by vacuum-deposition, vapor coating, chemical-deposition, or electroless plating. A variety of metals may be used to provide a reflective layer. These include aluminum, silver, chromium, nickel, magnesium, and the like, in elemental form. Aluminum and silver are the typically used metals in the

reflective layer. It is to be understood that in the case of aluminum, some of the metal may be in the form of the metal oxide and/or hydroxide. Aluminum and silver metals are desirable because they tend to provide good retroreflective brightness. The reflective layer should be thick enough to reflect incoming light. Typically, the reflective layer is about 50 to 150 nanometers thick. Although the reflective color of a silver coating can be brighter than an aluminum coating, an aluminum reflective layer is typically used.

In lieu of a metal layer, a dielectric mirror may be used as a specularly reflective layer. The dielectric mirror may be similar to known dielectric mirrors disclosed in U.S. Pat. Nos. 3,700,305 and 4,763,985 to Bingham.

In general, the sheeting material is prepared by embedding substantially a monolayer of retroreflective elements such as glass microspheres into a carrier web to a depth not exceeding 50% of the diameter of each microsphere; depositing specularly reflecting material over the retroreflective element-bearing surface of the carrier web; coating the binder composition of this disclosure over the specularly reflecting deposit; applying thermal energy to the binder composition to form a thermoplastic or thermosetting binder layer; and stripping away the carrier web while leaving the retroreflective elements partially embedded in the binder layer.

Referring to Figure 1, the exemplary retroreflective sheet article, **100**, has a carrier web, **10**, which may be paper, fabric, film or other material. Carrier web **10** has a coating, **20**, which may be polyethylene for example in which are at least partially embedded beads, **30**, which may be any transparent beads such as glass beads. Beads **30** have a reflective layer, **40**, such as a metal coating or a polymeric reflector, functionally disposed on the side of the beads opposite to the coating **20** and the carrier web **10**. The reflective coating may be disposed on the beads and it may at least partially cover a portion of the bead surface. The beads **30** are at least partially embedded in the binder, **50**, which may have polyurethane composition. The reflective layer **40** may be disposed between the binder **50** and the beads **30**. Other suitable intermediate layers may also be disposed therebetween. The binder **50** typically is 100-600 micrometers thick, or even 200-400 micrometers thick. Figure 2 shows the exemplary retroreflective sheet article, **200**, which is the same construction as in Figure 1 in which the carrier web, **10**, with coating, **20**, has been removed.

The binder composition may be either a mixture of the diisocyanate, polyisocyanate, polyol, unsaturated polyol, chain extension agent and any desired additives such as catalysts, pigments and the like; or it may be a polyurethane prepolymer mixture. If a prepolymer mixture is used, generally the mixture contains 2 parts, Part A and Part B. Typically Part A contains the reaction product of a diisocyanate, polyisocyanate, polyol and unsaturated polyol, and Part B contains one or more chain extension agents. Typically Part A and Part B are combined and mixed prior to application. The binder composition can be discharged or coated onto the beaded support web. The thermal curing process for the polyurethane is generally carried out at temperatures of about 70 to about 180° C, using an oven or other heating techniques. In some instances heating may be carried out at temperatures of about 70 to about 150° C. The cure rate may also be accelerated by using a catalyst as above described, if desired.

It is well understood in the polyurethane art that the properties of a polyurethane polymer can be varied by varying the composition and content of the isocyanate and hydroxyl reactive species used to make the polyurethane polymer. Typically the binder composition contains a mole ratio of isocyanate groups: hydroxyl groups of from 0.7 : 1 to 1.5 : 1. More typically the binder composition contains an isocyanate: hydroxyl ratio of from 1 : 1 to 1.3 : 1.

Typically the polyurethane binder comprises 30-60 percent by weight hard segment. The “hard segment” and “soft segment” concept is one that is well understood in the polyurethane art. In the present disclosure, hard segment elements are the diisocyanate, polyisocyanate, chain extension agents and any polyols with functionality greater than 2 while the soft segment elements are the polyols which are diols.

Retroreflective vulcanized rubber articles are prepared by co-vulcanizing a retroreflective sheet which comprises a plurality of retroreflective elements at least partially embedded in a polyurethane binder with an unvulcanized rubber. The polyurethane binder comprises unsaturated groups which may co-vulcanize with the unvulcanized rubber during the vulcanization process to form, for example, a tire.

The unvulcanized rubber used to make the co-vulcanized retroreflective rubber article generally is an uncured elastomer which is made from various elastomer-forming monomers. One class of such monomers are the various conjugated dienes having from 4

to 12 carbon atoms. Specific examples of monomers include butadiene, isoprene, pentadiene, hexadiene, heptadiene, octadiene, 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-pentadiene, and the like. An example of such an elastomer is natural rubber. By the term “natural rubber”, it is meant, the elastomeric substance obtained from various trees and plants which generally grow in the tropics or desert portions of the world. Such material contains a very high content (in excess of 90% and often in excess of 95%) of cis-1,4-isoprene. Also included within the class of conjugated dienes are various copolymers and interpolymers thereof.

Other classes of uncured elastomers may also be used. Some of these elastomers are classified as “synthetic rubbers” since they are not obtained from trees or plants. One class of useful elastomers are those prepared from monomers of conjugated dienes having 4 to 12 carbon atoms as described above and vinyl-substituted aromatic compounds containing from 8 to 15 carbon atoms. Examples of vinyl-substituted aromatic compounds include styrene, alphas-methyl styrene, 4-t-butyl styrene, vinyl toluene, divinyl benzene, isopropenyl benzene, di-isopropenyl benzene and the like. Some examples of copolymers in this class include SBR (poly(styrene-butadiene)), poly(alphas-methyl styrene-butadiene) and poly (4-t-butyl-styrene-butadiene). Another class of synthetic rubbers are the butyl rubbers. Butyl rubbers are copolymers of isobutylene with small amounts of isoprene. Neoprene is another synthetic rubber which may be used. Neoprene rubber is polychloroprene (2-chloro-1,3-butadiene). Another class of synthetic rubbers are the nitrile rubbers. The nitrile rubbers are copolymers of dienes with 4 to 12 carbon atoms as described above with acrylonitrile monomers.

The specific rubber or rubbers used will vary depending upon the style and type of use for the rubber article. For example when the rubber article is a bicycle tire, typically a mixture of natural rubber and synthetic rubber is used. In some embodiments, the rubber is a mixture of 75% natural rubber and 25% synthetic rubber, however, the percentages of natural and synthetic rubber may vary in particular applications.

Typically the unvulcanized rubber contains one or more vulcanizing agents capable of crosslinking the elastomeric rubber and co-vulcanizing with the unsaturated groups on the polyurethane binder of the retroreflective sheet. Typically the vulcanizing agent is present in an amount of less than about 0.25 weight percent. Typical vulcanization agents include sulphur or sulphur containing compounds such as, for

example, mercaptobenzothiazole and N-cyclohexyl-2 benzothiazolesulfenamide, or may contain a peroxide vulcanization agent. Peroxide vulcanization agents include, for example, classes such as peroxyesters, diacyl peroxides, dialkyl peroxides, and peroxyketals. Additionally, in some instances, vulcanization can be carried out with gamma radiation.

The preparation of reflective rubber articles is achieved through the co-vulcanization of a retroreflective sheet with unvulcanized rubber. The articles are prepared from retroreflective sheeting which contains retroreflective elements and a polyurethane binder. The polyurethane binder contains unsaturated groups which can co-vulcanize with the unvulcanized rubber to form the rubber article. In some embodiments the rubber article is a tire, such as a bicycle tire.

The retroreflective sheeting is contacted with unvulcanized rubber such that the side of the retroreflective sheeting which does not contain the retroreflective elements contacts the unvulcanized rubber. This contact can be effected in a variety of ways. One technique, which is useful in the manufacture of tires is the use of a mold. The molding equipment and methods useful for making and curing tires is well known to those in the tire making art. Typically the retroreflective sheeting and the unvulcanized rubber are placed in the mold and an expandable interior mold bladder is expanded using steam or other such pressure to cause the retroreflective sheeting and the unvulcanized rubber to expand into the mold with the retroreflective elements of the retroreflective sheeting facing the inner surface of the mold. Further expansion of the mold bladder causes the retroreflective sheeting and unvulcanized rubber to conform to the shape of the mold thereby creating the desired tire shape, texture and tread pattern. The bladder is retained in place by the pressure for a predetermined period of time during which the retroreflective sheeting and unvulcanized rubber are co-vulcanized by heat and pressure transmitted to the bladder by steam or other well known methods. The outer surface of the mold may also be heated to aid the co-vulcanization.

Upon removal of the tire article from the mold the retroreflective brightness of the formed tire is measured. In some embodiments the retroreflective brightness is at least 50% of the brightness of the retroreflective sheet prior to the vulcanization process. In other embodiments the retroreflective brightness is 80% of the brightness of the retroreflective sheet prior to the vulcanization process. Also, the retroreflective brightness

of the retroreflective elements in the formed tire are in some embodiments 250 cpl (cpl stands for candelas per lux per square meter). In other embodiments the retroreflective brightness of the retroreflective elements in the formed tire are 400 cpl.

Referring to Figure 3 which shows an exemplary embodiment of the vulcanized rubber article, **300**, of this disclosure. Beads, **30**, are at least partially embedded in polyurethane binder, **50**. A reflective coating, **40**, is disposed between the beads **30** and the polyurethane binder **50**. Polyurethane binder **50** is bonded to vulcanized rubber portion or layer **60**. Although the layer **60** is shown as a planar article, those of ordinary skill in the art will readily appreciate that the layer **60** may be curved, or, generally, it may be any desired shape and size. The figure is also not drawn to scale.

EXAMPLES

These examples are merely for illustrative purposes only and are not meant to be limiting on the scope of the appended claims. All parts, percentages, ratios, etc. in the examples and the rest of the specification are by weight, unless noted otherwise. Solvents and other reagents used were obtained from Sigma-Aldrich Chemical Company; Milwaukee, Wisconsin unless otherwise noted.

Table of Abbreviations

<u>Abbreviation or Trade Designation</u>	<u>Description</u>
DESMOPHEN C 1200	Polycarbonate diol with an approximate molecular weight of 2,000 commercially available from Bayer MaterialScience, Leverkusen, Germany
DESMOPHEN X 2501	Polycarbonate diol with an approximate molecular weight of 1,000 commercially available from Bayer MaterialScience, Leverkusen, Germany
HTPB 2800	Hydroxyl-terminated polybutadiene with an approximate molecular weight of 2,800
1,4-BDO	1,4-butanediol

DESMODUR I	Isophorone diisocyanate commercially available from Bayer MaterialScience, Leverkusen, Germany
DESMODUR VL	Aromatic polyisocyanate based on diphenylmethane diisocyanate commercially available from Bayer MaterialScience, Leverkusen, Germany
DESMODUR NZ1	Aliphatic polyisocyanate commercially available from Bayer MaterialScience, Leverkusen, Germany
FOMREZ UL 29	Tin catalyst commercially available from GE Silicones
REGAL 99R	Carbon black commercially available from Cabot
BICAT Z	Bismuth-zinc catalyst commercially available from Shepherd Chemical Company
KH-560	Silane coupling agent (3 glycidyloxypropyl) trimethoxy silane
Unvulcanized Rubber	Unvulcanized rubber containing natural rubber and sulfur vulcanizing agent used in the preparation of bicycle tires.
Temporary Support Film	A paper sheet with a polyethylene coating used a temporary support layer for microsphere beads.

Test Methods

Retroreflective Brightness

5 Retroreflectivity measurements for each of the following sheet materials were obtained using a retroluminometer according to the test method ASTM E808-81. The data are reported in candelas per lux per square meter (cpl).

Adhesion to Rubber

10 The adhesion of the retroreflective sheeting to rubber was tested by covering half of the surface area of the urethane side of the sheeting with a polyethylene terephthalate (PET) film. The PET film is to prevent that portion of the sheeting from bonding with the rubber surface. The resulting sheet was contacted with unvulcanized rubber and the resulting laminate was placed in a plate mold where it was cured at 180°C with a pressure of 15 Newtons for 5 minutes. After vulcanization the PET film was removed and the

sample was cut into strips. The peel strength was measured according to ASTM D 1876-95 T-Peel Test using the unbonded portion of the strip to start the peel front.

Example 1:

5 In a vessel DESMOPHEN C 1200, DESMOPHEN X 2501, HTPB 2800, and 1,4-BDO in the amounts shown in Table 1 were mixed for 30 minutes at 500 rpm. To this mixture was added DESMODUR I, DESMODUR VL, FOMREZ UL 29 in the amounts shown in table 1 and the resulting mixture was stirred for 30 minutes at 500 rpm. The mixture was coated onto a web containing aluminum-vapor-coated glass beads embedded
10 in a temporary support film, at a coating thickness of 300 micrometers. The coated sheet was placed in a 125°C oven for 30 minutes and then allowed to anneal for 2 days in a 65°C oven. The sheeting was stripped from the temporary support film and the Retroreflective Brightness was measured (Initial Retroreflective Brightness), the Adhesion to Rubber test was carried out, and the Retroreflective Brightness test was again carried
15 out (Post Vulcanization Retroreflective Brightness) using the test methods described above. The results are shown in Table 2.

Example 2:

20 The same procedure used for Example 1 above was followed with the amounts of reagents shown in Table 1. The results are shown in Table 2.

Table 1

Reagent	Example 1	Example 2
DESMOPHEN C 1200 (parts by weight)	25.04	9.00
DESMOPHEN X 2501 (parts by weight)	9.74	16.00
HTPB 2800 (parts by weight)	14.90	30.56
1,4-BDO (parts by weight)	11.72	9.34
DESMODUR I (parts by weight)	27.31	24.18
DESMODUR VL (parts by weight)	9.71	9.34
FOMREZ UL 29	50	50

(parts per million)		
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Comparative Example C1:

The same procedure described for Example 1 was followed except instead of the experimental retroreflective sheeting prepared in Example 1, the commercially available product 3M SCOTCHLITE 8150 was used. The results are shown in Table 2.

Table 2

Test	Example 1	Example 2	Comparative Example C1
Initial Retroreflective Brightness (cpl)	444	459	480
Post Vulcanization Retroreflective Brightness (cpl)	268	263	400
Adhesion to Rubber (N/mm)	3.20	3.84	1.80

Example 3:

Part A Preparation:

In a vessel DESMOPHEN C 1200, HTPB 2800, DESMODUR I, DESMODUR VL and REGAL 99R in the amounts shown in Table 3 were mixed for 3 hours at 1,000 rpm.

Part B Preparation:

In a vessel 1,4-BDO, BYK 359 and BICAT Z in the amounts shown in Table 3 were mixed for 30 minutes at 500 rpm.

Mixing, Coating and Curing:

Part A and Part B prepared above were mixed in an online mixer and coated to a thickness of 400 micrometers on a web containing aluminum-vapor-coated glass beads embedded in a temporary support film. The coated sheet was placed in a 165°C oven for 30 minutes and then allowed to anneal for 2 hours in a 150°C oven. The sheeting was stripped from the temporary support film and the Retroreflective Brightness was measured (Initial Retroreflective Brightness), the Adhesion to Rubber test was carried out, and the Retroreflective Brightness test was again carried out (Post Vulcanization Retroreflective Brightness) using the test methods described above. The results are shown in Table 4.

Table 3

Reagent	Part A (parts by weight)	Part B (parts by weight)
DESMOPHEN C 1200	43.40	----
HTPB 2800	8.00	----
DESMODUR I	29.00	----
DESMODUR VL	4.69	----
REGAL 99R	4.95	----
1,4-BDO	----	8.68
BYK 359	----	1.00
BICAT Z	----	0.29

Table 4

Test	Example 3	Comparative Example C1
Initial Retroreflective Brightness (cpl)	450	480
Post Vulcanization Retroreflective Brightness (cpl)	270	400
Adhesion to Rubber (N/mm)	>1.20	1.80

Examples 4-9:

Part A Preparation:

In a vessel DESMOPHEN C 1200, DESMOPHEN X 2501, HTPB 2800, DESMODUR I, DESMODUR VL, DESMODUR NZ1 and FOMREZ UL 29 in the amounts shown in Table 5 were mixed for 5 hours at 500 rpm.

Part B Preparation:

In a vessel 1,4-BDO, Glycerol, FOMREZ UL 29 and KH-560 in the amounts shown in Table 5 were mixed for 15 minutes at 100 rpm.

5 Mixing, Coating and Curing:

Part A and Part B prepared above were mixed and stirred for 15 minutes at 500 rpm and then was coated to a thickness shown in Table 6 on a web containing aluminum-vapor-coated glass beads embedded in a temporary support film. The coated sheet was placed in a 125°C oven for 30 minutes and then allowed to anneal for 2 days in a 65°C
10 oven. The sheeting was stripped from the temporary support film and the Retroreflective Brightness was measured (Initial Retroreflective Brightness), the Adhesion to Rubber test was carried out, and the Retroreflective Brightness test was again carried out (Post Vulcanization Retroreflective Brightness) using the test methods described above. The results are shown in Table 7.

15 Table 5: Part A

Reagent	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
DESMOPHEN C 1200 (parts by weight)	9.00	7.25	0	0	0	0
DESMOPHEN X 2501 (parts by weight)	16.00	16.91	26.75	24.53	24.64	24.64
HTPB 2800 (parts by weight)	30.56	29.53	26.75	24.53	24.64	24.64
DESMODUR I (parts by weight)	24.18	23.69	26.66	25.81	25.93	25.93
DESMODUR VL (parts by weight)	9.34	0	10.30	0	0	0
DESMODUR NZ1 (parts by weight)	0	13.65	0	15.71	15.78	15.78

FOMREZ UL 29 (parts per million)	0	150	0	150	150	150
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Table 6: Part B

Reagent	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
1,4-BDO (parts by weight)	9.34	8.97	9.55	9.42	7.89	7.89
Glycerol (parts by weight)	0	0	0	0	1.13	1.13
FOMREZ UL 29 (parts per million)	50	100	50	150	150	150
KH-560 (parts by weight)	0	0	0	0	0	0.5

Table 7

Test	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Thickness (micrometers)	300	280	320	260	350	350
Initial Retroreflective Brightness (cpl)	459	450	461	445	506	518
Post Vulcanization Retroreflective Brightness (cpl)	263	301	265	322	412	394
Adhesion to Rubber (N/mm)	----	----	----	----	5.8	5.4

What is claimed is:

1. A vulcanized rubber article comprising:
a vulcanized rubber portion; and
a retroreflective sheeting element comprising:
5 a polyurethane binder layer with first and second surfaces; and,
a plurality of retroreflective elements at least partially embedded in the first
surface;
wherein the second surface of the polyurethane binder layer is directly bonded to
the vulcanized rubber portion.
10
2. The article of claim 1, wherein the vulcanized rubber article is a tire.
3. The article of claim 1, wherein the polyurethane binder layer is the reaction
product of at least one diisocyanate, at least one polyisocyanate, at least one polyol, at
15 least one unsaturated polyol, and at least one chain extension agent.
4. The article of claim 3 where the polyol is a polycaprolactone diol, a polycarbonate
diol, a polyoxyalkylene diol, a polyurethane diol, a polyester diol or mixtures thereof.
- 20 5. The article of claim 4 further comprising a polyol with a functionality greater than
2.
6. The article of claim 3 wherein the unsaturated polyol is a hydroxyl terminated
polybutadiene.
25
7. The article of claim 3 wherein the chain extension agent is a diol with a number
average molecular weight of less than 120.
8. The article of claim 3 further comprising a silane coupling agent.
30
9. The article of claim 1, wherein the retroreflective brightness of the retroreflective
element is at least 250 cpl.

10. A method of making a vulcanized rubber article comprising:
providing a retroreflective sheeting element comprising:
a polyurethane binder layer with first and second surfaces
5 having unsaturated sites for co-vulcanization, and a plurality of
retroreflective elements partially embedded in the first surface;
contacting the second surface of the polyurethane binder layer with
unvulcanized rubber material; and
vulcanizing the unvulcanized rubber material under heat and pressure such that the
10 second surface of the binder layer of the retroreflective sheeting element is
bonded to the vulcanized rubber material.
11. The method of claim 10 wherein contacting the second surface of the binder layer
with unvulcanized rubber comprises:
15 placing the retroreflective sheeting element into a mold; and
introducing unvulcanized rubber material into the mold such that it contacts the
second surface of the binder layer.
12. The method of claim 10, wherein the brightness of the retroreflective sheet after
20 vulcanization is at least 50% that of the sheet before vulcanization.
13. The method of claim 10, wherein the polyurethane binder layer is the reaction
product of at least one diisocyanate, at least one polyisocyanate, at least one polyol, at
least one unsaturated polyol, and at least one chain extension agent.
25
14. The method of claim 13 further comprising a polyol with a functionality greater
than 2.
15. The method of claim 13 wherein the unsaturated polyol is a hydroxyl terminated
30 polybutadiene.
16. The method of claim 13 further comprising a catalyst.

17. The method of claim 11 wherein the polyurethane binder layer is the reaction product of a two part reaction mixture wherein the first part comprises:

5 a polyurethane prepolymer comprising at least one diisocyanate, at least one polyisocyanate, at least one polyol, and at least one unsaturated polyol; and the second part comprises at least one chain extension agent.

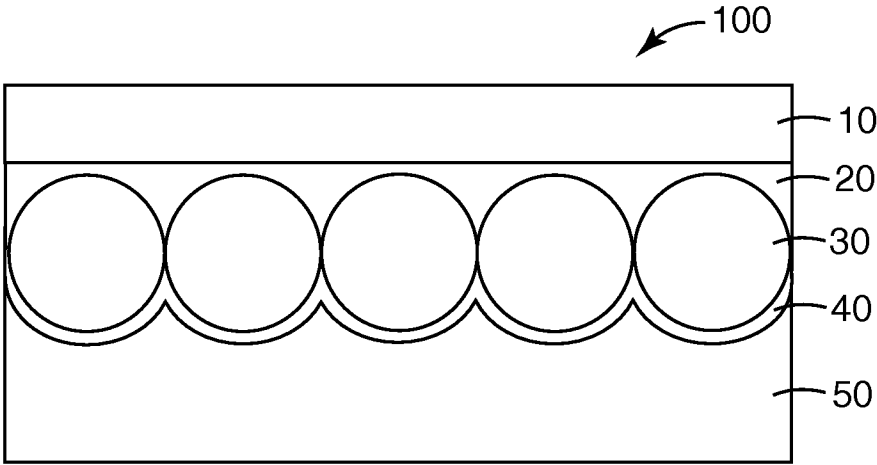


Fig. 1

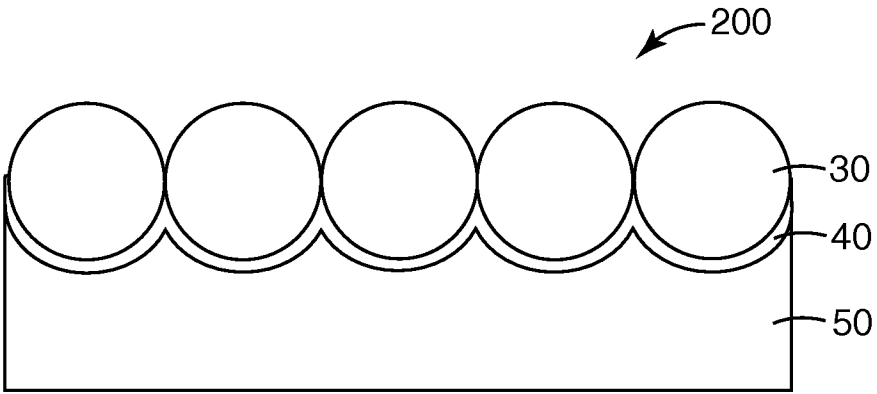


Fig. 2

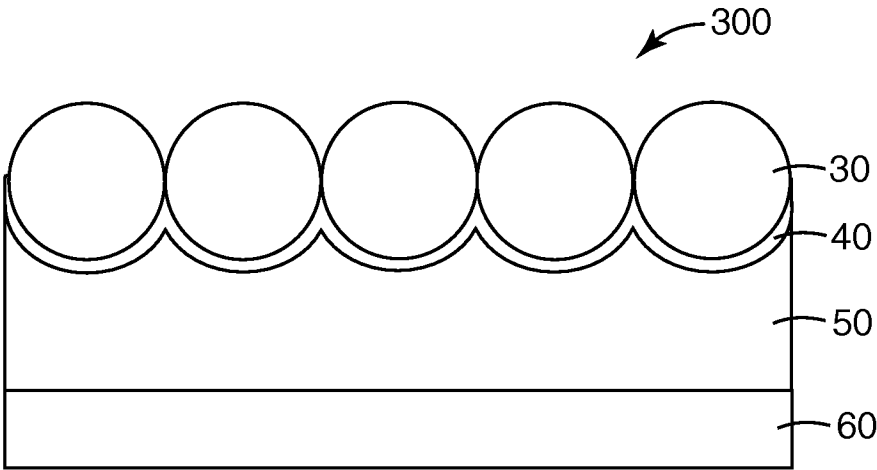


Fig. 3