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(54) Title: THERMOSET RUBBERS CONTAINING FUNCTIONALIZED POLYOLEFINS

(57) **Abstract:** The invention relates to members for use in vehicle sealing systems comprising a rubber support, which includes a functionalized polyolefin, and a surface layer adhered to the support, wherein the functionalized polylefin reduces discoloration of the surface layer.

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THERMOSET RUBBERS CONTAINING FUNCTIONALIZED POLYOLEFINS

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BACKGROUND OF INVENTION

Field of Invention

This invention relates generally to cured rubber, comprising at least one functionalized polyolefin, and the use thereof to control discoloration of the surface layers of vehicle sealing systems.

Background of Related Art

Recent general trends in motor vehicles, particularly automobiles, show that consumers demand better quality equipment compared to the automobiles available during the first three-quarters of the 20th century. Carmakers, therefore, are putting more emphasis on the visual aspects of certain components of automobiles, particularly the sealing systems.

Automobile sealing systems serve cosmetic purposes, by improving the aesthetic appearance of the car, and practical purposes, such as permitting glass to slide against the seal and providing insulation to air, water, and noise. Examples of vehicle sealing systems include those that function as glass run channels, door seals, and belt line seals. Sealing systems generally include components such as profiles and moldings. In some cases, the profiles and moldings include a fully or partially cured rubber component. The rubber is typically an ethylene--alpha-olefin--diene monomer terpolymer, and more specifically an ethylene-propylene-diene monomer terpolymer (EPDM) because EPDM has a higher resistance than other rubbers to degradation caused by exposure to ultraviolet (UV) light, heat, ozone, and/or oxygen.

Complex seal designs can be facilitated by the addition of thermoplastic elastomeric parts at the extremities of a seal, or by joining two different rubber profiles with a thermoplastic elastomeric part. Additional materials can also be adhered on the surface or at the extremity of a rubber profile to improve insulation, service life, and appearance. For example, a colored thermoplastic veneer that matches the color of other plastic trim in the automobile and additionally includes a thermoplastic elastomer can be adhered to the surface of a typical black rubber profile.

Discoloration problems have been encountered with sealing systems such as those that include a rubber component adhered to a colored thermoplastic veneer. The discoloration is the result of curative residues migrating through the thermoplastic material and reacting due to exposure to environmental conditions, such as but not limited to heat, ozone, oxygen, and/or light, particularly ultraviolet (UV) or infrared (IR) light, to cause surface staining. There is a commercial need, therefore, for a rubber material, which may be coated, that can reduce or eliminate the discoloration of vehicle sealing systems, even after aging in hostile environments.

SUMMARY OF INVENTION

The present invention relates to a member for use in a sealing system comprising a) a support including a rubber component and from about 1 to about 50 parts per hundred rubber (phr), based on the total weight of the rubber component, of a functionalized polyolefin, and b) a surface layer adhered to the support. The functionalized polyolefin includes a functionality selected from acids, anhydrides, epoxides, amines, hydroxyls, and combinations thereof.

The invention further relates to a method for reducing the discoloration of a multi-layer polymer component, particularly in an automobile sealing system.

DETAILED DESCRIPTION OF INVENTION

By the present invention, it has been discovered that a support for use in a vehicle sealing system that includes a rubber component and a functionalized polyolefin surprisingly and unexpectedly reduces the discoloration of a surface layer adhered thereto, thus improving the aesthetics of a vehicle. Vehicles contemplated include, but are not limited to passenger automobiles, trucks of all sizes, farm vehicles, trains, and the like.

The Support

The term "support" for the purposes of this application is meant to include extruded and molded rubber profiles generally for use as vehicle sealing systems, such as, but not limited to glass run channels, door seals, and belt line seals.

The support preferably comprises a rubber component and from about 1 to about 50 phr, based on the total weight of the rubber component, of a functionalized polyolefin. For purposes of this application, "phr" references will be based on the total rubber component of the support. The rubber component can be a single rubber or a blend of two or more different rubbers.

The rubber component and functionalized polyolefin, along with other materials such as but not limited to reinforcing materials, diluting fillers, curing agents, accelerators, and other additives which would be well known to those of ordinary skill in the art, may be combined in a rubber mill, an internal kneader, such as a Banbury mixer or the like, or in other suitable rubber mixing apparatus. The resulting compound is subject to further processing, such as, but not limited to one or more of extrusion, compression molding, transfer molding, injection molding, and curing using apparatus, times, and temperatures well known to those skilled in the art. Curing can take place in a heated mold cavity or in a continuous heat transferring device, such as, but not limited to a hot air oven, possibly coupled with a microwave oven or bath containing a heated liquid salt medium. Preferably, the compound is compression molded and cured at 180° C to be fully cured. Fully cured is intended to mean that the cured parts are thermoset, meaning that the cured part cannot be replasticized and is not melt reprocessable.

Those of ordinary skill in the art will appreciate the appropriate amounts of curative, types of cure systems, and cure conditions required to carry out the curing. Preferred cure systems include, but are not limited to sulfur-based systems, metal oxides, phenolic resin systems, maleimides, peroxide-based systems, high-energy radiation, and combinations thereof, both with and without accelerators and co-agents. Examples of the mixed peroxide-type or mixed sulfur-type curing systems employed include [dicumylperoxide plus 2,5-bis-(tert-butylperoxy)-2,5-dimethyl-hexane] and [sulfur plus tetramethylthiuramidisulfide plus dicumyl peroxide]. Preferably, the support is cured by a sulfur-based curative, peroxide-based curative, or a combination thereof. More preferably, the support is cured by a sulfur-based curative, such as, but not limited to thiuram disulfides (tetramethylthiuramdisulfide) and thiomorpholines (dithiodimorpholine) in an amount of from 0 to about 10 phr, based on the total weight of the rubber component. Reference may be had to "Vulcanization and Vulcanizing Agents," W. Hoffman, Palmerton Publishing Co., New York, 1967, for an extensive disclosure of curing methods and curing agents.

As in conventional practice, an accelerator of sulfur curing may be used to reduce the curing time by increasing the speed of the crosslinking reaction. Typical accelerators include, but are not limited to thiazoles (2-mercaptobenzothiazole, mercaptobenzothiazol disulfide), guanidines (diphenylguanidine), sulfenamides (n-cyclohexylbenzothiazolsulfenamide), dithiocarbamates (zincdimethyldithiocarbamate), thioureas (1,3 diethylthiourea), and others well known by those skilled in the art. The accelerator can be used in the range of from 0 to about 5 phr, based on the total weight of the rubber component. Activators, such as, but not limited to zinc oxide and stearic acid, may be used to activate the accelerators and attain good crosslink density. Typical quantities of zinc oxide and stearic acid are from 0 to about 20 phr, based on the total weight of the rubber component.

Other materials may be added in addition to the curative, accelerator, and activator. Such materials include, but are not limited to carbon black, processing oils, mineral fillers, and processing aids. The preferred carbon black is generally produced from the combustion of a gas and/or a hydrocarbon feed and has a particle size of from about 20nm to 100nm for the regular furnace or channel black or from about 150nm to about 350nm for the thermal black. The level of carbon black in the support may range from about 10 to about 300 phr, based on the total weight of the rubber component. The processing oil, preferably paraffinic, is added to adjust the viscosity of the support for good processing. Preferably, the level of processing oil in the compound is from 0 to about 200 phr, based on the total weight of the rubber component. Mineral filler, typically calcium carbonate used in quantities of from 0 to about 150 phr, based on the total weight of the rubber component, can be used to dilute the support. Other mineral fillers can be used as reinforcing fillers, such as, but not limited to silica, aluminum silicate, magnesium silicate, and others well known by those skilled in the art. Processing aids can also be used, such as, but not limited to polyethylene glycol, having a molecular weight from about 100 to about 10,000, in an amount of from 0 to about 10 phr, based on the total weight of the rubber component.

The degree of cure of the cured support can be described in terms of either gel content or extractable components. Where the determination of extractable components is an appropriate measure of the degree of cure, the support preferably contains no more than about 4 weight percent extractables at room temperature, approximately 25° C, by a solvent, such as, but not limited to hexane. More preferably, the support contains no more than 2 weight percent extractables, and even more preferably contains essentially no extractables from the cured phase, essentially no extractables meaning less than 0.5 weight percent. In general, less rather than more extractables is preferred.

The support of the present invention may be modified by adding other ingredients that are conventional in curing. Such ingredients include particulate fillers, clay, colored pigments, reinforcing agents, stabilizers, antioxidants, flame retardants, tackifiers, plasticizers, waxes, and extender oils.

Rubber Component

The term "rubber" for the purposes of this application is considered to encompass all elastomeric polymers and plastics, such as but not limited to ethylene--alpha-olefin--diene monomer terpolymer, particularly EPDM; ethylene propylene rubber (EPR); butyl rubber; halobutyl rubber; styrene-isoprene-styrene (SIS); styrene-butadiene copolymers (SBC); polyisoprene rubber; polyisobutylene rubber (PIB); styrene-butadiene-styrene (SBS); styrene-butadiene rubber (SBR); polybutadiene rubber (BR); blends of said elastomeric polymers, as well as blends of these rubbers with thermoplastics. The preferred rubber component of the support is a polymer derived from ethylene, one or more alpha-olefins, and one or more non-conjugated diene monomers. The preferred ethylene content is from about 35 to about 85 weight percent, based on the total weight of the ethylene--alpha-olefin--diene monomer terpolymer, preferably from about 40 to about 80 weight percent, and more preferably from about 45 to about 75 weight percent.

The diene monomer can be one or more non-conjugated dienes containing 30 carbon atoms or less, more preferably 20 carbon atoms or less. The preferred non-conjugated dienes include, but are not limited to one or more of 5-ethylidene-2-norbornene (ENB); 1,4-hexadiene; 1,6-octadiene; 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; vinylnorbornene; dicyclopentadiene; and combinations thereof. The preferred non-conjugated diene content is from about 1 to about 15 weight percent, based on the total weight of the ethylene--alpha-olefin--diene monomer terpolymer, and preferably from about 2 to about 11 weight percent.

Alpha-olefin will make up the remainder of the ethylene--alpha-olefin--diene monomer terpolymer, with percentages adding up to 100 weight percent. The preferred alpha-olefins include, but are not limited to C_3, C_4, C_6, C_8, and higher molecular weight alpha-olefins. More preferably, the alpha-olefin is propylene.

Ethylene--alpha-olefin--diene monomer terpolymers can be prepared using a conventional polymerization process, including traditional Ziegler-Natta catalysts, as well as metallocene catalysts. Synthesis of ethylene--alpha-olefin--diene monomer terpolymers is well known in the art. Reference may be had to G. ver Strate, Encyclopedia of Polymer Science and Engineering, vol. 6, 2nd Ed., 1986, pp. 522-564.

In one embodiment, the rubber component is Vistalon™ 8700 available from ExxonMobil Chemical Company, Baytown, Texas. Vistalon™ 8700 is a polymer of ethylene-propylene-ethylidene norbornene having an ethylene content of about 63 weight percent and an ethylidene norbornene content of about 8 weight percent.

Functionalized Polyolefin

The term "functionalized polyolefin" for the purposes of this application is considered to include all polymers derived from olefins and functionalities. Such functionalities include, but are not limited to acids, anhydrides, epoxides, amines, and hydroxyls.

In one embodiment, the functionalized polyolefin is present in the support in an amount sufficient to control discoloration. Preferably, the functionalized polyolefin is present in an amount of from 1 to 50 phr, based on the total weight of the rubber component. However, the lower limit is preferably at least 5 phr, more preferably at least 10 phr, and even more preferably at least 20 phr. The upper limit is preferably not greater than 40 phr, more preferably not greater than 30 phr, and even more preferably not greater than 20 phr. The functionalized polyolefin is distinguished from the ethylene--alpha-olefin--diene monomer terpolymer by the substantial absence of diene in the functionalized polyolefin, substantial absence meaning less than 1 weight percent.

Functionalized polyolefins can be prepared using conventional Ziegler-Natta catalyst systems or metallocene-based catalyst systems. The preferred polyolefin of the support is a copolymer derived from ethylene and one or more alpha-olefins. Preferably, ethylene is present in an amount of from about 5 to about 90 weight percent, based on the total weight of the functionalized polyolefin, and more preferably from about 10 to about 80 weight percent.

The preferred components that provide functionalization include, but are not limited to acids, anhydrides, epoxides, amines, hydroxyls, and combinations thereof. Preferably, the functionalization component is present in an amount of from about 0.1 weight percent to about 5 weight percent, based on the total weight of the functionalized polyolefin, and more preferably at least about 0.5 weight percent.

Alpha-olefin will make up the remainder of the functionalized polyolefin, with percentages adding up to 100 weight percent. The preferred alpha-olefins include, but are not limited to propylene, butene-1, 4-methyl-1-pentene, hexene-1, octene-1, higher molecular weight alpha-olefins, and combinations thereof.

In one embodiment, the functionalized polyolefin is selected from Exxelor™ MDEX 94-8 and Exxelor™ MDEX 97-2, both of which are available from ExxonMobil Chemical Company, Baytown, Texas. Exxelor™ MDEX 94-8 is an ethylene-octene copolymer containing about 30 mmole/gram of maleic anhydride functionality. Exxelor™ MDEX 97-2 is an ethylene-octene copolymer containing about 30 mmole/gram of hydroxyl functionality.

Functionalization can occur by reacting the polyolefin with an unsaturated organic compound. This functionalization may be accomplished by any technique known in the art, such as those disclosed in U.S. Patent No. 3,236,917; U.S. Patent

No. 4,950,541; and U.S. Patent No. 5,194,509, which are incorporated herein by reference for purposes of U.S. patent practice. Typically, the polyolefin to be grafted, the unsaturated organic compound and an optional free radical initiator are all introduced into a reaction zone, heated or mixed, and allowed to react. One of the many possible methods to graft an ethylene--alpha-olefin copolymer would be introducing the copolymer into a mixing device, such as a single or twin screw extruder or an internal mixer, heating the copolymer until it is molten, injecting the unsaturated organic compound and the free radical initiator into the mixing device, and mixing the components under high or low shear conditions. The unsaturated organic compounds may be added as a neat compound, as part of a master batch, or as a supported compound. The supporting compound is typically a polymer but may be any of the well-known inorganic supporting compounds.

In one embodiment, the unsaturated organic compounds contemplated are those containing at least one unsaturation and at least one carbonyl group (-C=O). Representative compounds include the carboxylic acids, anhydrides, esters and their salts, both metallic and non-metallic. Preferred compounds are compounds containing an α, β-unsaturated conjugated carbonyl group. Preferred examples include maleic, fumaric, acrylic, methacrylic, itaconic, crotonic, alpha-methyl crotonic and cinnamic acids, their anhydride, ester and salt derivatives, as well as glycidylmethacrylate, glycidyl acrylate or other glycidyl compounds, hydroxyalkyl acrylates, hydroxyalkyl methacrylates, vinylpyridine, vinylpyrrolidone and vinyl pyrrole. Maleic anhydride is a preferred unsaturated organic compound.

Illustrative of the free radical initiators include well-known peroxides, such as dialkyl peroxides, e.g., dicumylperoxide, 2,5-dimethyl-2,5-bis-(tert-butylperoxy) hexyne-3, tert-butylcumylperoxide, and 2,5-dimethyl-2,5-bis-(tert-butylperoxy) hexane; diacylperoxides, e.g., dibenzoyl peroxide and dilauryl peroxide; peroxyesters, e.g., tert-butylperoxyacetate and tert-butylperoxypivalate; peroxyketones; monoperoxycarbonates; and azo compounds, e.g., azobisisobutyronitrile (AIBN). Commercially available peroxides of these families are the Lupersol™ and Luperox™ products, available from Atofina Chemicals, Inc., Philadelphia, Pennsylvania; and the Trigonox™ and Perkadox™

products, available from Akzo Nobel Chemicals, Amersfoort, Netherlands.

In another embodiment, the functionalized polyolefins are the product of post reaction of the maleic anhydride functionalized polyolefins with other chemicals containing amines, alcohols, thioalcohols or epoxides, as described in U.S. Patent No. 5,424,367. A detailed list of reactants is given in this patent, which is incorporated herein by reference for purposes of U.S. patent practice.

In yet another embodiment, functionalization occurs by direct polymerization of ethylene, propylene, or a higher alpha-olefin comonomer, and a functionalized diene. As polar groups are poisons of Ziegler-Natta catalysts, the functional groups have to be protected through reaction with triethyl aluminum prior to polymerization and the protective groups have to be removed via acidic hydrolysis. This technology allows synthesizing ethylene--alpha-olefin copolymer containing carboxylic acid groups, hydroxyl groups and amines, as described in U.S. Patent No. 4,987,200, which is incorporated herein by reference for purposes of U.S. patent practice.

In still another embodiment, the functionalized polyolefin is produced by polymerization of ethylene, alpha-olefin, selected olefinic ester, carboxylic acids and other monomers with selected transition metal compounds, as described in PCT publication WO 96/23010, which is incorporated herein by reference for purposes of U.S. patent practice.

Surface Layer

For purposes of this application, the term "surface layer" is meant generally and is considered to encompass any material suitable for use on the surface of sealing system components. Suitable materials can be sprayed onto the support and/or adhered to the support by heat and pressure, co-extrusion, or molding. Examples of suitable materials include, but are not limited to silicone, polyurethane, thermoplastic elastomers, and thermoset elastomers. Preferably, the thickness of the surface layer ranges from about 0.1 mm to about 10 mm.

Preferably, the coating is a thermoset elastomer or a thermoplastic elastomer, with a thermoplastic elastomer (TPE) being more preferred. A TPE is generally defined herein as a polymer or blend of polymers that can be processed and recycled in the same way as a conventional thermoplastic material, yet has functional properties and performance similar to that of a conventional thermoset rubber. Polymer blends that have a combination of both thermoplastic and elastic properties are generally obtained by combining a thermoplastic polyolefin with an elastomeric composition in a way such that the elastomer is intimately and uniformly dispersed as a discrete particulate phase within a continuous phase of the thermoplastic. Shaped articles may be formed from thermoplastic elastomers by processes, such as, but not limited to extrusion, injection molding, and compression molding.

TPEs contemplated for the invention include, but are not limited to styrene block copolymers, polyolefin blends, thermoplastic polyamides, thermoplastic polyurethanes, thermoplastic copolyesters, and elastomeric alloys. Descriptions of various types of TPEs may be found in Modern Plastics Encyclopedia 1988, Vol. 64, No. 10A, pp. 93-100 (October 1987), and in Modern Plastics Encyclopedia 1990, Vol. 66, No. 11, pp. 122-131 (Mid-October 1989), both incorporated herein by reference for purposes of U.S. patent practice.

Preferably, the TPE is a blend of a partially or fully cured elastomer and a polyolefin. More preferably, the TPE is a blend of dynamically vulcanized elastomer dispersed in a matrix of thermoplastic polyolefin.

The process of dynamically vulcanizing an elastomer in a polyolefin matrix is well known in the art. Early work found in U.S. Pat. No. 3,037,954, hereby incorporated by reference for purposes of U.S. patent practice, discloses the technique of dynamic vulcanization, wherein a vulcanizable elastomer is dispersed into a resinous thermoplastic polymer and the elastomer is cured in the presence of a curative while continuously mixing and shearing the polymer blend. The resulting composition, called dynamically vulcanized alloy or thermoplastic vulcanizate (TPV), is a microgel dispersion of cured elastomer in an uncured matrix of thermoplastic polymer. Further general background information is found in EP 473,703, EP 657,504, WO 95/26380(A1), the disclosures of which are hereby incorporated by reference for purposes of U.S. patent practice.

The elastomers suitable for use in the manufacture of the TPE include, but are not limited to one or more elastomers selected from monoolefinic copolymer rubbers, such as ethylene-propylene rubber (EPR); unsaturated monoolefin rubbers, such as EPDM; butyl rubbers, such as copolymers of an isoolefin and a conjugated monoolefin, terpolymers of an isoolefin with or without a conjugated monoolefin, divinyl aromatic monomers and the halogenated derivatives of such copolymers and terpolymers; a copolymer of a C_4-C_7 isomonoolefin and a para-C_1-C_6-alkylstyrene and a halogenated derivative thereof; natural rubber; synthetic polyisoprene; polybutadiene rubber; styrene-butadiene-copolymer rubbers; blends of any of the above olefinic rubbers; nitrile rubbers; and polychloroprene rubber. Preferably, the elastomer is an EPDM.

The polyolefins suitable for use in the manufacture of the TPE include but are not limited to those prepared from monoolefin monomers having 2 to 7 carbon atoms, such as ethylene, propylene, 1-butene, isobutylene, 1-pentene, 1-hexene, 1-octene, 3-methyl-1-pentene, 4-methyl-1-pentene, 5-methyl-1-hexene, and the like, mixtures thereof, and copolymers thereof. More preferably, the polyolefin is selected from isotactic polypropylene and ethylene-propylene copolymer. The polyolefins can be made by conventional Ziegler-Natta catalyst systems or by metallocene-based catalyst systems.

In addition to the elastomer and polyolefin, other ingredients may be present, such as, but not limited to particulate fillers, clay, calcium carbonate, silica, talc, titanium dioxide, carbon black, colored pigments, zinc oxide, stearic acid, reinforcing agents, stabilizers, antioxidants, flame retardants, tackifiers, plasticizers, wax, and extender oils, lubricants, anti-blocking agents, anti-static agents, foaming agents, and other processing aids known in the rubber compounding art.

In one embodiment of the invention, the TPE is a TPV comprising a blend of about 25 to about 75 weight percent, based on the total weight of the TPV, of polypropylene and about 75 to about 25 weight percent, based on the total weight of the TPV, of EPDM, with the percentages adding up to 100 percent, and wherein the EPDM may be fully cured. Such a TPV is sold under the trademark Santoprene™, which is available from Advanced Elastomer Systems, St. Louis, Missouri.

General Uses of the Member

Certain embodiments of the invention provide improved properties, particularly resistance to discoloration. In the absence of the functionalized polyolefins of this invention, EPDM with a thermoplastic rubber coating has been found to experience undesirable levels of discoloration upon exposure to light. Such products have been tested by exposure to severe climates, such as those encountered in Florida, or in artificial laboratory aging under UV or infrared light. After exposure, the products are analyzed using apparatus for testing the effect of weather on the surface of objects, such as the Weather-OMeter™ available from Atlas Electric Devices Co., Chicago, Illinois, and the Xenotest™, available from W.C. Heraeus GMBH, Hanau, Federal Republic of Germany.

The products tested are comprised of a thermoset rubber with a light colored thermoplastic or thermoset veneer adhered thereto for aesthetic purposes. Some of those veneers were found to have been severely discolored. It is contemplated that such discoloration has been caused, at least in part, by the migration of chemical species present in the thermoset rubber part. The chemical species are believed to move through the veneer and react with the light, causing unacceptable discoloration and staining of the lightly colored veneer. Accordingly, certain specific embodiments of this invention provide improvements in the area of resistance to discoloration. Examples of such improvement in resistance to discoloration are discussed below.

EXAMPLES

Table 1 illustrates the test methods used in the following examples.

TABLE 1

Parameter	Units	Test
Mooney Viscosity*	ML1+4, 125° C, MU	ASTM D 1646
(elastomeric polymer content determination)* Ethylene	Weight %	ASTM D 3900
Ethylidene Norbornene	Weight %	ASTM D 6047
Mooney Viscosity (compound)	ML1+4, 100° C, MU	ASTM D 1646
Mooney Relaxation (MLR)	MU.sec.	ASTM D 1646
Mooney Scorch time	Ts_2, 125°C, minutes	ASTM D 1646
Moving Die Rheometer (MDR) @ 180° C,± 0.5°arc ML MH Ts2 T_{90} Cure rate	dN.m dN.m minute minute dN.m/minute	ASTM D 2084
Physical Properties, press cured 10 minutes @ 180° C Hardness 100% Modulus Tensile Strength Elongation at Break	Shore A MPa MPa %	ISO 7619-1986 ISO 37 - 1977 type 2 ISO 37 - 1977 type 2 ISO 37 - 1977 type 2
Compression Set, press cured 8 min. @ 180° C 22 hrs / 70° C/25%deflection	%	ISO 815-1972(E)
Tear Resistance	kN/m	DIN 53 507 A
Color Spectrum Analyze Hunterlab 10° observation, D65 light Yellow index, E		ASTM D 1925

In the following examples, three different thermoset EPDM compounds were prepared. Compound I included only Vistalon™ 8700 EPDM, and was included in the tests as a reference for comparison purposes. Compound II was an admixture of Vistalon™ 8700 EPDM and 5 phr of Exxelor™ MDEX 94-8. Compound III was an admixture of Vistalon™ 8700 EPDM and 5 phr of Exxelor™ MDEX 97-2. The other ingredients in those compounds, and their respective amounts, are reported in Table 2.

TABLE 2

Compound Batch	Compound I	Compound II	Compound III
EPDM Vistalon™ 8700	115	115	115
Exxelor™ MDEX 97-2 (hydroxyl)	0	5	0
Exxelor™MDEX 94-8 (maleic anhydride)	0	0	5
Spheron™ 5000 carbon black	130	130	130
Omya™ BSH calcium carbonate	50	50	50
Plastol™ 537 plasticizer	55	55	55
Carbowax™ 4000 PEG	2	2	2
Zinc Oxide active	1	1	1
Stearic Acid	1	1	1
Rhenogran™ Calcium Oxide 80%	6	6	6
Sulfur	1.3	1.3	1.3
MBT (75%)	1.6	1.6	1.6
Rhenocure™ TP/G (50%)	1.8	1.8	1.8
ZDEC (70%)	0.7	0.7	0.7
Vulkalent™ EC	0.7	0.7	0.7
Total Weight	366.1	371.1	371.1

Each of the three compounds was compression molded at 180 C° to fully cure. The cure characteristics are reported in Table 3.

TABLE 3

Rheology	Thermoset reference	Modified thermoset	Modified thermoset

	compound I	compound II	compound III
Mooney Viscosity ML 1+4, 100°C	61	65	65
MDR +/- 1° arc - 180°C			
ML, dN.m	2.2	2.5	2.3
MH, dN.m	26	26	27
Ts_2, minute	0.53	0.57	0.55
T90, minute	3.2	3.6	3.2
Cure Rate, dN.m/minute	30.4	28.3	30

Next, a veneer of thermoplastic elastomer, Santoprene™ 221-79, available from Advanced Elastomer Systems of St. Louis, Missouri, colored in beige and containing an anti-UV package, was adhered to each of the rubber surfaces, by action of heat and pressure, to provide composite members. Each of the three composite members was exposed for up to 1000 hours to artificial UV and IR light at 70° C. The results of the various tests are reported in Table 4.

TABLE 4

Elastomeric rubber		Thermoset reference compound I	Modified thermoset compound II	Modified thermoset compound III
Thermoplastic elastomer		Santoprene 221-79 W 233	Santoprene 221-79 W 233	Santoprene 221-79 W 233
Staining test at 70°C				
"E" change	24 h	2.1	0.1	0.1
	168 h	2.9	0.1	0.3
	500 h	3.8	0.1	0.3
	1000h	5.8	0.1	0.1

Only Compound I, the reference sample, showed yellow staining, whereas Compounds II and III, the two compounds containing either hydroxyl groups or maleic anhydride functionality, did not have visual traces of discoloration. The thermoplastic veneer alone, not adhered to any thermoset rubber, does not discolor after a similar aging test (E index variation < 0.2, "E" being the expression of a yellow index calculated from color spectrum analysis). Visual observation was quantitatively confirmed by laboratory spectral measurements showing a strong increase of the yellow component, meaning an E index variation > 4, of the color spectrum of thermoplastic rubber veneer when in contact with the reference thermoset EPDM Compound I. With Exxelor™ modified thermoset compound, the E index variation stays below 0.3.

The results reported in Table 4 were confirmed by another test using a different thermoplastic elastomer, Santoprene™ 8221-70, having by its composition a better color stability than the Santoprene™ 221-79. The yellow index (E) increased to a lesser extent, but showed a similar trend with better color stability for a thermoset compound containing Exxelor™. The results thereof are reported in Table 5.

TABLE 5

Elastomeric rubber		Thermoset reference compound I	Modified thermoset compound II	Modified thermoset compound III
Thermoplastic elastomer		Santoprene 8221-70	Santoprene 8221-70	Santoprene 8221-70
Staining test at 70°C				
"E" change	24 h	0.25	0.17	0.22
	168 h	0.31	0.13	0.17
	500 h	0.48	0.13	0.2
	1000h	0.55	0.31	0.33

It was discovered that the addition of Exxelor™ at a level of 5 phr in the rubber thermoset compound had very little to no effect on the rubber curing performance. Rubber curing performance is important in keeping a high productivity in the manufacture of dense sealing profile extrusion cured by a continuous process such as UHF-hot air channel. Rubber curing performance is also critical for the elastic properties of the finished profiles.

CONCLUSION

While the present invention has been described in considerable detail with reference to certain preferred versions thereof, other versions are possible. For example, while the compositions described herein are preferably used for or with automobile sealing systems, other uses are not excluded. Also, different types of members and configurations of members can be formed in accordance with the invention, in a number of different ways that will be apparent to persons having ordinary skill in the art. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred versions contained herein.

CLAIMS

What is claimed is:

1. A member for use in a sealing system comprising:

   a) a support comprising a rubber component and from about 1 to about 50 phr, based on the total weight of the rubber component, of a functionalized polyolefin, and

   b) a surface layer adhered to said support.

2. The member of claim 1, wherein the support is cured.

3. The member of claim 2, wherein the support is sulfur-cured.

4. The member of claim 2, wherein the functionalized polyolefin comprises a functionality selected from acids, anhydrides, epoxides, amines, and hydroxyls.

5. The member of claim 2, wherein the functionalized polyolefin comprises a functionality selected from maleic anhydride and hydroxyls.

6. The member of claim 4, wherein the functionality is present in an amount of from about 0.1 to about 5 weight percent, based on the total weight of the functionalized polyolefin.

7. The member of claim 4, wherein the functionality is present in an amount of from about 0.5 to about 5 weight percent, based on the total weight of the functionalized polyolefin.

8. The member of claim 2, wherein the rubber component comprises an ethylene--alpha-olefin--diene monomer terpolymer.

9. The member of claim 8, wherein the alpha-olefin of the terpolymer is propylene.

10. The member of claim 8, wherein the diene is selected from one or more of 5-ethylidene-2-norbornene (ENB); 1,4-hexadiene; 1,6-octadiene; 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; vinylnorbornene; dicyclopentadiene; and combinations thereof.

11. The member of claim 9, wherein the diene is selected from one or more of 5-ethylidene-2-norbornene (ENB); 1,4-hexadiene; 1,6-octadiene; 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; vinylnorbornene; dicyclopentadiene; and combinations thereof.

12. The member of claim 10, wherein the ethylene content is from about 35 to about 85 weight percent and the diene content is from about 1 to about 15 weight percent, based on the total weight of the ethylene--alpha-olefin--diene monomer terpolymer.

13. The member of claim 2, wherein the functionalized polyolefin is present in an amount of from about 5 to about 40 phr, based on the total weight of the rubber component.

14. The member of claim 2, wherein the functionalized polyolefin is present in an amount of from about 10 to about 30 phr, based on the total weight of the rubber component.

15. The member of claim 2, wherein the functionalized polyolefin is present in an amount of about 20 phr, based on the total weight of the rubber component.

16. The member of claim 2, wherein the functionalized polyolefin comprises an ethylene--alpha-olefin copolymer.

17. The member of claim 4, wherein the functionalized polyolefin comprises an ethylene--alpha-olefin copolymer.

18. The member of claim 16, wherein the alpha-olefin of the copolymer is selected from propylene, butene-1, 4-methyl-1-pentene, hexene-1, octene-1, and combinations thereof.

19. The member of claim 16, wherein the alpha-olefin of the copolymer is octene.

20. The member of claim 2, wherein the surface layer comprises a material selected from one or more of silicone, polyurethane, thermoplastic elastomer, and thermoset elastomer.

21. The member of claim 2, wherein the surface layer is a thermoplastic elastomer.

22. The member of claim 21, wherein the thermoplastic elastomer is selected from one or more of a styrene block copolymer, a polyolefin blend, a thermoplastic polyamides, a thermoplastic polyurethane, a thermoplastic copolyester, and an elastomeric alloy.

23. The member of claim 21, wherein the thermoplastic elastomer is a blend of a dynamically vulcanized elastomer dispersed in a matrix of thermoplastic polyolefin.

24. The member of claim 23, wherein the dynamically vulcanized elastomer is an ethylene-propylene-diene monomer terpolymer (EPDM) and the thermoplastic polyolefin is selected from polypropylene and ethylene-propylene copolymer.

25. The member of claim 20, wherein the surface layer has a thickness of from about 0.1mm to about 10mm.

26. The member of claim 2, wherein the sealing system is selected from a glass run channel, door seal, and belt line seal.

27. A member for reducing the discoloration of a multilayer polymer component comprising:

a) a cured support comprising an ethylene-propylene-diene monomer terpolymer (EPDM) and from about 1 to about 50 phr, based on the total weight of the EPDM, of a functionalized ethylene--alpha-olefin copolymer, wherein the functionalized ethylene--alpha-olefin copolymer comprises a functionality selected from acids, anhydrides, epoxides, amines, and hydroxyls.

b) a surface layer adhered to said support, wherein the surface layer comprises a material selected from one or more of silicone, polyurethane, thermoplastic elastomer, and thermoset elastomer.

28. The member of claim 27, wherein the support is sulfur-cured.

29. The member of claim 27, wherein the functionalized ethylene--alpha-olefin copolymer comprises a functionality selected from maleic anhydride and hydroxyls.

30. The member of claim 29, wherein the functionality is present in an amount of from about 0.5 to about 5 weight percent, based on the total weight of the functionalized polyolefin.

31. The member of claim 27, wherein the functionalized ethylene--alpha-olefin copolymer is present in an amount of from about 10 to about 30 phr, based on the total weight of the rubber component.

32. The member of claim 27, wherein the functionalized ethylene--alpha-olefin copolymer is present in an amount of about 20 phr, based on the total weight of the rubber component.

33. The member of claim 27, wherein the alpha-olefin of the copolymer is selected from propylene, butene-1, 4-methyl-1-pentene, hexene-1, octene-1, and combinations thereof.

34. The member of claim 27, wherein the alpha-olefin of the copolymer is octene.

35. The member of claim 27, wherein the surface layer is a thermoplastic elastomer.

36. The member of claim 35, wherein the thermoplastic elastomer is a blend of a dynamically vulcanized elastomer dispersed in a matrix of thermoplastic polyolefin.

37. The member of claim 36, wherein the dynamically vulcanized elastomer is an ethylene-propylene-diene monomer terpolymer (EPDM) and the thermoplastic polyolefin is a material selected from polypropylene and ethylene-propylene copolymer.

38. The member of claim 27, wherein the surface layer has a thickness of from about 0.1mm to about 10mm.

39. The member of claim 27, wherein said surface layer is adhered to said support by one or more processes selected from coextrusion, overmolding, heat sealing, extrusion coating, spraying, and combinations thereof.

40. The member of claim 27, wherein said multilayer polymer component is a vehicle sealing system.

41. The member of claim 40, wherein said vehicle sealing system is selected from a glass run channel, door seal, and belt line seal.

42. A method of reducing the discoloration of a multilayer polymer component comprising:
    a) providing a cured support comprising an ethylene-propylene-diene monomer terpolymer (EPDM) and from about 5 to about 40 phr, based on the total weight of the EPDM, of a functionalized ethylene--alpha-olefin copolymer, wherein the functionalized ethylene--alpha-olefin copolymer comprises a functionality selected from acids, anhydrides, epoxides, amines, and hydroxyls; and
    b) adhering a surface layer comprising a material selected from one or more of silicone, polyurethane, thermoplastic elastomer, and thermoset elastomer to said support by one or more processes selected from coextrusion, overmolding, heat sealing, extrusion coating, spraying, and combinations thereof.

43. The method of claim 42, wherein the support is sulfur-cured.

44. The method of claim 42, wherein the functionalized ethylene--alpha-olefin copolymer comprises a functionality selected from maleic anhydride and hydroxyls.

45. The method of claim 42, wherein the functionality is present in an amount of from about 0.5 to about 5 weight percent, based on the total weight of the functionalized polyolefin.

46. The method of claim 42, wherein the cured support comprises an EPDM and about 20 phr, based on the total weight of the EPDM, of a functionalized ethylene--alpha-olefin copolymer.

47. The method of claim 42, wherein the alpha-olefin of the copolymer is selected from propylene, butene-1, 4-methyl-1-pentene, hexene-1, octene-1, and combinations thereof.

48. The method of claim 42, wherein the alpha-olefin of the copolymer is octene.

49. The method of claim 42, wherein the surface layer is a thermoplastic elastomer.

50. The method of claim 49, wherein the thermoplastic elastomer is a blend of a dynamically vulcanized elastomer dispersed in a matrix of thermoplastic polyolefin.

51. The method of claim 50, wherein the dynamically vulcanized elastomer is an ethylene-propylene-diene monomer terpolymer (EPDM) and the thermoplastic polyolefin is a material selected from polypropylene and ethylene-propylene copolymer.

52. The method of claim 42, wherein the surface layer has a thickness of from about 0.1mm to about 10mm.

53. The method of claim 42, wherein the multilayer polymer component is a vehicle sealing system.

54. The method of claim 53, wherein said vehicle sealing system is selected from a glass run channel, door seal, and belt line seal.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/20575

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B32B 27/32
US CL : 428/492, 519, 520, 521, 522

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 428/492, 519, 520, 521, 522

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EAST: (polypropylene, polyolefin or polyethylene) + rubber + (graft$ or modif$)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,296,554 A (WATANABE et al.) 22 March 1994 (22-03-1994)	1-54
A	US 5,041,338 A (SUEHIRO et al.) 20 August 1991 (20-08-1991)	1-54
A	US 5,424,135 A (MURATA et al.) 13 June 1995 (13-06-1995)	1-54
A	US 5,534,590 A (HORIIE) 09 July 1996 (09-07-1996)	1-54

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier application or patent published on or after the international filing date		
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"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

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