



- (51) International Patent Classification:  
*C08L 9/00* (2006.01)
- (21) International Application Number:  
PCT/US2012/043134
- (22) International Filing Date:  
19 June 2012 (19.06.2012)
- (25) Filing Language: English
- (26) Publication Language: English
- (71) Applicants (*for all designated States except US*): **THE YOKOHAMA RUBBER CO., LTD.** [JP/JP]; 36-11, Shimbashi 5-chome, Tokyo, 1058685 (JP). **EXXON-MOBIL CHEMICAL PATENTS INC.** [US/US]; 13501 Katy Freeway, Houston, TX 77079 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **HARA, Yuichi** [JP/JP]; C/o The Yokohama Rubber CO., LTD, Hiratsuka Factory, 2-1, Oiwake, Hiratsuka-shi, Kanagawa, 254-8601 (JP). **SATO, Shun** [JP/JP]; C/o The Yokohama Rubber CO., LTD, Hiratsuka Factory, 2-1, Oiwake, Hiratsuka-shi, Kanagawa, 254-8601 (JP). **BLOK, Edward, J.** [US/US]; 154 Durling Drive, Wadsworth, OH 44281 (US). **ELLUL, Maria, D.** [US/US]; 3230 N. Dover Road, Silver Lake Village, OH 44224-2422 (US). **DIAS, Anthony, J.** [US/US]; 918 Noble Springs Road, Houston, TX 77062 (US). **RANDAL, Kerstetter, Howard, III** [US/US]; 157 W. North Street, Wadsworth, OH 44281 (US).
- (74) Agent: **AMERNICK, Burton, A.**; Connolly Bove Lodge & Hutz LLP, 1875 Eye Street, NW, Suite 1100, Washington, DC 20006 (US).
- (81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:  
— with international search report (Art. 21(3))

(54) Title: THERMOPLASTIC ELASTOMER COMPOSITION AND PROCESS TO PRODUCE SAME

(57) Abstract: Disclosed herein is a thermoplastic elastomer composition having improved uv and processability, comprising a post-vulcanized dynamically vulcanized alloy (DVA) and a low molecular weight aromatic amine stabilizer, wherein the DVA comprises an isobutylene elastomeric component dispersed as a domain in a continuous phase comprising at least one thermoplastic resin. A method to produce the thermoplastic elastomer composition is also disclosed.



THERMOPLASTIC ELASTOMER COMPOSITION  
AND PROCESS TO PRODUCE SAME

**FIELD OF THE INVENTION**

[0001] The present invention relates to dynamically vulcanized alloys (DVAs) and in particular to DVAs having improved processability and stability. The invention also relates to methods for making the DVAs.

**BACKGROUND OF THE INVENTION**

[0002] Compositions comprising a DVA, which may also be referred to in the art as a thermoplastic vulcanizate, often includes reinforcing fillers to improve various properties of the composition including mechanical properties and UV resistance.

[0003] One of the major drawbacks of reinforcing fillers is their negative impact on processing and other properties of the composition. Higher filler loading, which may be required to provide adequate UV resistance, is associated with higher viscosity, which may result in process issues and concerns.

[0004] Several approaches have been attempted to increase the UV resistance for the DVA films. When UV stabilizers were added directly to the DVA during preparation of the DVA, the stabilizers had a tendency to also act as a cure accelerator - resulting in scorching of the rubber. To resolve the scorching problem, US 7459212 discloses adding stabilizers to an adjacent rubber layer and relying on migration of the stabilizer into the DVA to achieve the desired properties. However, it is not always desirable to have such an adjacent rubber layer next to the DVA when used as an innerliner due to an increase in the innerliner weight.

[0005] Accordingly, a need exists for elastomeric compositions having improved UV resistance and/or processing properties, and methods to produce such compositions.

**SUMMARY OF THE INVENTION**

**[0006]** In an aspect of the present disclosure a thermoplastic elastomer composition comprises a post-vulcanized dynamically vulcanized alloy (DVA) and a low molecular weight aromatic amine stabilizer, wherein the DVA comprises an isobutylene elastomeric component dispersed as a domain in a continuous phase comprising at least one thermoplastic resin.

**[0007]** In another aspect of the present disclosure, a process to produce a thermoplastic elastomer composition comprises post-vulcanization mixing a DVA, with a low molecular weight aromatic amine stabilizer, wherein the DVA comprises an isobutylene elastomeric component dispersed as a domain in a continuous phase comprising at least one thermoplastic resin.

**[0008]** In still another aspect of the present disclosure, a process to produce a thermoplastic elastomer composition comprises dynamically vulcanizing an isobutylene elastomeric component dispersed as a domain in a continuous phase comprising at least one thermoplastic resin to produce a post-vulcanization DVA; and mixing the post-vulcanization DVA with a low molecular weight aromatic amine stabilizer to produce the thermoplastic elastomer composition.

**[0009]** In yet another aspect of the present disclosure, a thermoplastic elastomer composition is prepared by a process comprising dynamically vulcanizing a halogenated isobutylene elastomeric component dispersed as a domain in a continuous phase comprising a polyamide to produce a post-vulcanization DVA; and mixing the post-vulcanization DVA with a low molecular weight aromatic amine stabilizer to produce the thermoplastic elastomer composition.

**[0010]** In another aspect of the present disclosure, a method to reduce the melt viscosity and improve the UV resistance of a DVA comprises mixing the DVA post-vulcanization, with a low molecular weight aromatic amine

stabilizer to produce a stabilized composition, wherein the DVA comprises an isobutylene elastomeric component dispersed as a domain in a continuous phase comprising at least one thermoplastic resin.

#### **DETAILED DESCRIPTION**

**[0011]** In an embodiment, the present disclosure is directed to a thermoplastic elastomer composition comprising a post-vulcanized dynamically vulcanized alloy (DVA) and a low molecular weight aromatic amine stabilizer, wherein the DVA comprises an isobutylene elastomeric component dispersed as a domain in a continuous phase comprising at least one thermoplastic resin. Also disclosed is a process to make the composition. In an embodiment, the viscosity of the composition is reduced to allow for inclusion of various fillers and other additives in amounts sufficient to provide desired levels of UV resistance and other physical properties, while having a viscosity low enough to provide improved processability of the composition.

**[0012]** In an embodiment, the DVA comprises a thermoset component dispersed as a domain in a continuous thermoplastic phase, which has been dynamically vulcanized. This DVA is referred to herein as a "post-vulcanized" composition, which is then mixed with the stabilizer to produce the thermoplastic elastomer composition.

**[0013]** As used herein, "polymer" may be used to refer to homopolymers, copolymers, interpolymers, terpolymers, etc. Likewise, a copolymer may refer to a polymer comprising at least two monomers, optionally with other monomers. When a polymer is referred to as comprising a monomer, the monomer is present in the polymer in the polymerized form of the monomer or in the derivative form of the monomer. However, for ease of reference the phrase comprising the (respective) monomer or the like is used as shorthand. Likewise, when catalyst components are described as comprising neutral stable forms of the

components, it is well understood by one skilled in the art, that the ionic form of the component is the form that reacts with the monomers to produce polymers.

**[0014]** Rubber refers to any polymer or composition of polymers consistent with the ASTM D1566 definition: "a material that is capable of recovering from large deformations, and can be, or already is, modified to a state in which it is essentially insoluble (but can swell) in boiling solvent." "Elastomer" is a term that may be used interchangeably with the term rubber.

"Elastomeric composition" refers to any composition comprising at least one elastomer as defined above.

**[0015]** A vulcanized rubber compound by ASTM D1566 definition refers to "a crosslinked elastic material compounded from an elastomer, susceptible to large deformations by a small force capable of rapid, forceful recovery to approximately its original dimensions and shape upon removal of the deforming force." A cured elastomeric composition refers to any elastomeric composition that has undergone a curing process and/or comprises or is produced using an effective amount of a curative or cure package, and is a term used interchangeably with the term vulcanized rubber compound.

**[0016]** A "thermoplastic elastomer" refers to a rubber-like material "that repeatedly can be softened by heating and hardened by cooling through a temperature range characteristic of the polymer, and in the softened state can be shaped into articles" as defined in ASTM D1566. Thermoplastic elastomers are microphase separated systems of at least two polymers. One phase is the hard polymer that does not flow at room temperature, but becomes fluid when heated, that gives the thermoplastic elastomer its strength. Another phase is a soft rubbery polymer that gives thermoplastic elastomers their elasticity. The hard phase is typically the major or continuous phase.

**[0017]** A thermoplastic vulcanizate by ASTM D1566 definition refers to "a thermoplastic elastomer with a

chemically cross-linked rubbery phase, produced by dynamic vulcanization". Dynamic vulcanization is the process of intimate melt mixing of a thermoplastic polymer and a suitable reactive rubbery polymer to generate a thermoplastic elastomer with a chemically cross-linked rubbery phase wherein the vulcanizable elastomer is vulcanized under conditions of high shear. As a result, the vulcanizable elastomer is simultaneously crosslinked and dispersed as fine particles, which have been described elsewhere as a "micro gel," within the engineering resin matrix.

**[0018]** Dynamic vulcanization is effected by mixing the ingredients at a temperature which is at or above the curing temperature of the elastomer in equipment such as roll mills, Banbury® mixers, continuous mixers, kneaders or mixing extruders, e.g., twin screw extruders. A unique characteristic of dynamically cured compositions is that, notwithstanding the fact that the elastomer component may be fully cured, the compositions can be processed and reprocessed by conventional thermoplastic resin processing techniques such as extrusion, injection molding, compression molding, and the like. Scrap or flashing can be salvaged and reprocessed.

**[0019]** In an embodiment, the thermoset component is an elastomeric component having a small particle size where the number average equivalent domain diameter ranges from 0.1 to 1 micron. In an embodiment, the continuous thermoplastic phase is a polyamide, also referred to as a nylons or nylons. Such compositions are particularly suited for use as vapor barriers in pneumatic tires, and the like.

**[0020]** In an embodiment, the elastomeric component comprises an isobutylene elastomer, preferably a halogenated isobutylene elastomer, more preferably a copolymer of isobutylene and para-alkylstyrene, such as described in European Patent No. 0344021 B1. As used herein, "isobutylene elastomer" or "isobutylene elastomer

component" refers to elastomers or polymers comprising at least 70 mole percent repeat units from isobutylene. The copolymers preferably have a substantially homogeneous compositional distribution. Preferred alkyl groups for the para-alkyl styrene moiety include alkyl groups having from 1 to 5 carbon atoms, primary haloalkyl, secondary haloalkyl having from 1 to 5 carbon atoms and mixtures thereof. A preferred copolymer comprises isobutylene and para-methylstyrene.

**[0021]** Suitable halogenated isobutylene elastomer components include copolymers (such as brominated isobutylene-paramethylstyrene copolymers) having a number average molecular weight  $M_n$  of at least about 25,000, preferably at least about 50,000, preferably at least about 75,000, preferably at least about 100,000, preferably at least about 150,000. The copolymers may also have a ratio of weight average molecular weight ( $M_w$ ) to number average molecular weight ( $M_n$ ), i.e.,  $M_w/M_n$  of less than about 10, preferably less than about 8, preferably less than about 6, preferably less than about 4, more preferably less than about 2.5, most preferably less than about 2.0. In another embodiment, suitable halogenated isobutylene elastomer components include copolymers (such as brominated isobutylene-paramethylstyrene copolymers) having a Mooney viscosity (1+4) at 125°C (as measured by ASTM D 1646-99) of 25 or more, preferably 30 or more, more preferably 40 or more.

**[0022]** In one embodiment, brominated copolymers of isobutylene and para-methylstyrene include those having 5 to 12 weight percent para-methylstyrene, 0.3 to 1.8 mol % brominated para-methylstyrene, and a Mooney viscosity of 30 to 65(1+4) at 125°C (as measured by ASTM D 1646-99).

**[0023]** In an embodiment, the halogenated isobutylene elastomer component can be prepared from isobutylene and about 0.5 to 25 percent by weight, preferably about 1 to 20 percent by weight, based upon the total amount of the comonomers, of p-alkylstyrene, preferably p-

methylstyrene, followed by halogenation. Typically, the slurry polymerization of the monomer mixture is carried out in the presence of a Lewis acid catalyst and the subsequent halogenation is carried out in the presence of a radical initiator such as heat and/or light or a chemical initiator in the form of a solution. The content of the halogen (e.g., Br and/or Cl, preferably Br) is preferably less than about 10 percent by weight, more preferably about 0.1 to about 7 percent by weight, based upon the total amount of the copolymer. In an embodiment, the preferred elastomeric component comprises an isobutylene elastomer, preferably a halogenated isobutylene elastomer, with brominated p-methylstyrene-co-isobutylene polymers (BIMS) being most preferred.

**[0024]** For purposes of the present invention, a thermoplastic (alternatively referred to as thermoplastic resin) useful in the present invention is a thermoplastic polymer, copolymer, or mixture thereof having a Young's modulus of more than 200 MPa at 23°C. The resin should have a melting temperature of about 170°C to about 260°C, preferably less than 260°C, and most preferably less than about 240°C. By conventional definition, a thermoplastic is a synthetic resin that softens when heat is applied and regains its original properties upon cooling.

**[0025]** Such thermoplastic resins may be used singly or in combination and generally contain nitrogen, oxygen, halogen, sulfur or other groups capable of interacting with an aromatic functional groups such as halogen or acidic groups. Suitable thermoplastic resins include resins selected from the group 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),



ethylene copolymer resins (EVA or EVOH) and mixtures thereof.

**[0026]** Suitable 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, pyrrolidione, 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). Commercially available 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. Copolymers Nylon 48, Nylon MXD6, Nylon 6/66 (N6/66), Nylon 610 (N610), Nylon 612 (N612) may also be used. The copolymers thereof and any blends thereof may also be used.

**[0027]** Additional examples of satisfactory polyamides include those having a softening point below 275°C, and others described in Kirk-Othmer, Encyclopedia of Chemical Technology, v. 10, page 919, and Encyclopedia of Polymer Science and Technology, Vol. 10, pages 392-414. 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°C-230°C being preferred.

**[0028]** In an embodiment, the polyamide is at least one member selected from the group consisting of Nylon 6, Nylon 66, Nylon 11, Nylon 69, Nylon 12, Nylon 610, Nylon 612, Nylon 6/66 and copolymers thereof.

**[0029]** Suitable 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 C<sub>2-6</sub> 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-cyclohexanedimethylene) oxlate and poly-(cis-1,4-cyclohexanedimethylene) succinate, poly (C<sub>2-4</sub> alkylene terephthalates) such as polyethyleneterephthalate and polytetramethylene-terephthalate, poly (C<sub>2-4</sub> 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 C<sub>2</sub> to C<sub>4</sub> diols, such as polyethylene terephthalate and polybutylene terephthalate. Preferred polyesters will have a melting point in the range of 160°C to 260°C.

**[0030]** Poly(phenylene ether) (PPE) 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.

**[0031]** Ethylene copolymer resins useful in the invention include copolymers of ethylene with unsaturated esters of lower carboxylic acids as well as the carboxylic acids per se. In particular, copolymers of ethylene with vinylacetate or alkyl acrylates for example

methyl acrylate and ethyl acrylate can be employed. These ethylene copolymers typically comprise about 60 to about 99 wt% ethylene, preferably about 70 to 95 wt% ethylene, more preferably about 75 to about 90 wt% ethylene. The expression "ethylene copolymer resin" as used herein means, generally, copolymers of ethylene with unsaturated esters of lower ( $C_1 - C_4$ ) monocarboxylic acids and the acids themselves; e.g. acrylic acid, vinyl esters or alkyl acrylates. It is also meant to include both "EVA" and "EVOH", which refer to ethylene-vinylacetate copolymers, and their hydrolyzed counterpart ethylene-vinyl alcohols.

**[0032]** In the DVA, the halogenated isobutylene elastomer comprises less than or equal to about 95 parts by weight per 100 parts by weight of the alloy, preferably from about 95 to 5 parts by weight of the alloy. In an embodiment, the elastomer is present in an amount of 5 to 80 parts by weight of the alloy. In an embodiment, the elastomer is present in an amount of 10 to 65 parts by weight of the alloy. In an embodiment, the amount of the thermoplastic resin is greater than or equal to about 5 parts by weight per 100 parts by weight of the alloy, preferably from about 5 to 95 parts by weight of the alloy. In one embodiment, the halogenated isobutylene elastomer comprises from 5 to 80 parts by weight and the polyamide comprises from 20 to 95 parts by weight, wherein the total parts by weight of the of the halogenated isobutylene elastomer and the polyamide totals 100.

**[0033]** The DVA may further comprise a vulcanization or cross-linking agent, a vulcanization or cross-linking accelerator, various types of oils, an anti-aging agent, reinforcing agent, plasticizer, softening agent, or other various additives generally mixed into general rubbers. The compounds are mixed and vulcanized by general methods to cross-link the composition. The amounts of these additives generally are known to one of skill in the art

and are selected so long as they do not run counter to the improvements observed with thermoplastic elastomer compositions according to the present disclosure.

**[0034]** The thermoplastic elastomeric composition may further comprise one or more composition additives including carbon black; fatty acids; waxes; antioxidants; curatives; calcium carbonate; clay; silica; talc; UV absorbers; UV stabilizers; antiozonants; ZnO; CuI; scorch inhibiting agents; anti-cling additives; tackifiers such as polybutenes, terpene resins, aliphatic and aromatic hydrocarbon resins, alkali metal and glycerol stearates and hydrogenated rosins; heat stabilizers; antiblocking agents; release agents; anti-static agents; pigments; colorants; dyes; or a combination thereof. Each or any of the composition additives may be present in the composition at less than or equal to about 50 phr, less than or equal to about 40 phr, less than or equal to about 30 phr, less than or equal to about 20 phr, less than or equal to about 10 phr, less than or equal to about 5 phr, less than or equal to about 3 phr, less than or equal to about 2 phr, or less than or equal to about 1.5 phr each of a composition additive.

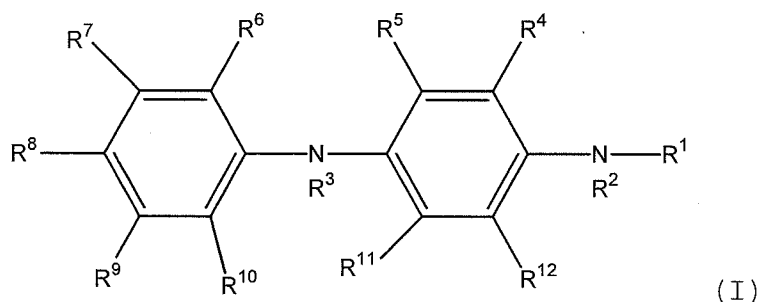
**[0035]** Suitable UV absorbers and UV stabilizers include hindered amine light stabilizers (HALS). In an embodiment, the HALS include amino and amino ether derivatives of 2,2,6,6-tetramethylpiperidine, and the like. In an embodiment, the HALS is an oligomeric hindered amine light stabilizer, e.g., TINUVIN (Ciba Specialty Chemicals, USA). Suitable antioxidants include hindered phenols. Examples include those sold under the trade name IRGANOX (BASF, USA). Suitable antioxidants/antiozonates include substituted amino triazines, including 2,4,6-Tris-(N-1,4-dimethylpentyl-p-phenylenediamino)-1,3,5-triazine, sold under the trade names DURAZONE 37, CHEMTURA, USA, and the like.

**[0036]** In an embodiment, the thermoplastic elastomeric composition may further comprise one or more

plasticizers. Examples include sulfonamide plasticizers including those sold under the trade name UNIPLEX, e.g., UNIPLEX 214 n-butylbenzene sulfonamide or BBSA (Unitex Chemical, USA), and the like.

**[0037]** In accordance with the invention, the thermoplastic elastomer composition comprises a DVA and a low-molecular weight aromatic amine stabilizer wherein the DVA and stabilizer are mixed as discussed herein. As used herein, "low molecular weight" refers to a compound having a number average molecular weight less than 1000 g/mol. The low-molecular weight aromatic amine stabilizer preferably has a molecular weight of less than or equal to about 500 g/mol.

**[0038]** An "aromatic amine stabilizer" refers to a low molecular weight compound having aromatic protons and at least one, preferably two or more, amine groups. In an embodiment, the low molecular weight aromatic amine stabilizer may have general formula (I):



wherein  $R_1$  is a  $C_1$  to  $C_{20}$  hydrocarbyl group and  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$ , and  $R^{12}$  are individually selected from H or  $C_1$ - $C_{20}$  hydrocarbyl groups. In one embodiment, any of  $R^2$  to  $R^{12}$  are individually selected from H or  $C_1$ - $C_{10}$  hydrocarbyl groups.

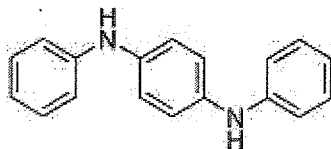
**[0039]** For purposes herein, the term "hydrocarbyl groups" refers to substituted or unsubstituted  $C_1$ - $C_{20}$  straight, branched and cyclic alkyl radicals,  $C_6$ - $C_{20}$  aromatic radicals,  $C_7$ - $C_{20}$  alkyl-substituted aromatic radicals, and  $C_7$ - $C_{20}$  aryl-substituted alkyl radicals, halogenated radicals, which may include various substituents. In addition two or more such radicals may

together form a fused ring system, including partially or fully hydrogenated fused ring systems. In an embodiment, the hydrocarbyl groups may be substituted or unsubstituted C<sub>1</sub>-C<sub>10</sub> straight, branched and cyclic alkyl radicals, C<sub>6</sub>-C<sub>10</sub> aromatic radicals, C<sub>7</sub>-C<sub>10</sub> alkyl-substituted aromatic radicals, and C<sub>7</sub>-C<sub>10</sub> aryl-substituted alkyl radicals, halogenated radicals, which may include various substituents. Representative hydrocarbyl substituents include mono-, di- and tri-substituted functional groups, also referred to herein as radicals, comprising a Group 14 element, wherein each of the hydrocarbyl groups contains from 1 to 20 carbon atoms. Examples of the various hydrocarbyl substituents include substituents comprising Group 15 and/or Group 16 heteroatoms. Examples include amines, phosphines, ethers, thioethers and/or derivatives thereof, e. g. amides, phosphides, per-ethers and/or thioether groups.

**[0040]** Other functional groups suitable for use as substituents include organic and inorganic radicals, wherein each of the functional groups comprises hydrogen, and atoms from Groups 13, 14, 15, 16, and/or 17, preferably 1 to 20 or 1 to 10 carbon atoms, oxygen, sulfur, phosphorous, silicon, selenium, or a combination thereof. In addition, functional groups may include one or more functional group substituted with one or more additional functional groups. Examples of functional group radicals include: hydrogen, hydroxyl, alkyl, alkyloxy, alkenyloxy, aryl, aryloxy, aralkyl, aralkyloxy, alkaryl, arylalkenyl, cycloalkyl, cycloalkyloxy, aliphatic, hydroxyl, alkanol, alkanolamine, oxy, acetyl, acetamido, acetoacetyl, acetonyl, acetonylidene, acrylyl, alanyl, allophanoyl, anisyl, benzamido, butryl, carbonyl, carboxy, carbazoyl, caproyl, capryl, caprylrl, carbamido, carbamoyl, carbamyl, carbazoyl, chromyl, cinnamoyl, crotoxyl, cyanato, decanoly, disiloxanoxy, epoxy, formamido, formyl, furyl, furfuryl, furfurylidene, glutaryl, glycinamido, glycolyl, glycyl, glyocylyl,

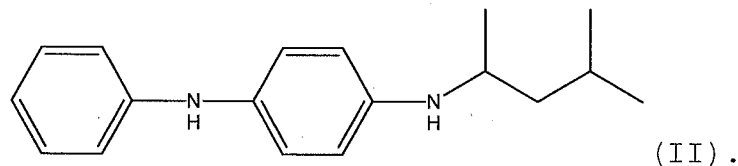
heptadecanoyl, heptanolyl, hydroperoxy, hydroxamino, hydroxylamido, hydrazido/hydrazide, hydroxy, iodoso, isocyanato, isonitroso, keto, lactyl, methacrylyl, malonyl, nitroamino, nitro, nitrosamino, nitrosimino, nitrosyllnitroso, nitrilo, oxamido, peroxy, phosphinyl, phosphide/phosphido, phosphite/phosphito, phospho, phosphono, phosphoryl, seleninyl, selenonyl, siloxy, succinamyl, sulfamino, sulfamyl, sulfeno, thiocarboxy, toluylyl, ureido, valeryl radicals, acetimido, amidino, amido, amino, aniline, anilino, arsino, azido, azino, azo, azoxy, benzylidene, benzidyne, biphenylyl, butylene, iso-butylene, sec-butylene, tert-butylene, cyano, cyanamido, diazo, diazoamino, ethylene, disilanyl, glycidyl, guanidino, guanyl, heptanamido, hydrazino, hydrazo, hypophosphito, imido, isobutylidene, isopropylidene, silyl, silylene, methylene, mercapto, methylene, ethylene, naphthal, naphthobenzyl, naphthyl, naphthylidene, propylene, propylidene, pyridyl, pyrrol, phenethyl, phenylene, pyridino, sulfinyl, sulfo, sulfonyl, tetramethylene, thenyl, thienyl, thiobenzyl, thiocarbamyl, thiocarbonyl, thiocyanato, thionyl, thiuram, toluidino, tolyl, a-tolyl, tolylene, a-tolylene, tosyl, triazano, ethenyl (vinyl), selenyl, trihydrocarbylamino, trihaloamino, trihydrocarbyl phosphite, trihalophosphine, trimethylene, trityl, vinylidene, xenyl, xylylidino, xylyl, xylylene, dienes, and combinations thereof.

**[0041]** In an embodiment, the low molecular weight aromatic amine stabilizer comprises a diaryl-p-phenylene diamine. An example of a diaryl-p-phenylene diamine includes a compound having the following formula:



In an embodiment, the aromatic amine stabilizer comprises N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine,

having formula (II):



**[0042]** The stabilizer is present in the thermoplastic elastomeric composition at greater than or equal to about 1 part per hundred of rubber by weight (phr), greater than or equal to about 1.5 phr, greater than or equal to about 2 phr, greater than or equal to about 2.5 phr, greater than or equal to about 3 phr, greater than or equal to about 3.5 phr, or greater than or equal to about 4 phr. Additionally, the stabilizer is present in the thermoplastic elastomeric composition at less than or equal to about 20 phr, less than or equal to about 10 phr, less than or equal to about 9 phr, less than or equal to about 8 phr, less than or equal to about 7 phr, less than or equal to about 6 phr, or less than or equal to about 5 phr. The stabilizer is mixed with the vulcanized DVA in amounts ranging from any of the above listed minimum parts by weight to any of the above listed maximum parts by weight.

#### **Process**

**[0043]** Per the invention, a process to produce a thermoplastic elastomer composition comprises post-vulcanization mixing a dynamically vulcanized alloy with a low molecular weight aromatic amine stabilizer, wherein the DVA comprises an isobutylene elastomeric component dispersed as a domain in a continuous phase comprising at least one thermoplastic resin.

**[0044]** In an embodiment, a process to produce a thermoplastic elastomer composition comprises dynamically vulcanizing an isobutylene elastomeric component dispersed as a domain in a continuous phase comprising at least one thermoplastic resin to produce a 'post-vulcanization DVA' followed by mixing the post-



vulcanization DVA with a low molecular weight aromatic amine stabilizer to produce the thermoplastic elastomer composition.

**[0045]** In an embodiment, the thermoplastic elastomer composition is produced by first heating the post-vulcanization DVA to a temperature above the glass transition or softening temperature of the alloy and then mixing the at least partially melted alloy under high shear conditions with the low molecular weight aromatic amine stabilizer, and optionally with other composition additives, plasticizers, and the like to produce the mixture or blend. In an embodiment, the mixture is a homogeneous mixture comprising the various components interdispersed with one another. By homogeneous mixture it is not intended that the mixture is a single phase, but instead is intended to represent a well blended mixture of the various materials present in the composition. In an embodiment, the mixing may be conducted via roll mills, BANBURY mixers, continuous mixers, kneaders, mixing extruders, e.g., twin screw extruders, combinations thereof, and/or the like.

**[0046]** In an embodiment, a method to reduce the viscosity and improve the UV resistance of a DVA comprises mixing the DVA post-vulcanization, with a low molecular weight aromatic amine stabilizer to produce a stabilized composition, wherein the DVA comprises an isobutylene elastomeric component dispersed as a domain in a continuous phase comprising a polyamide. As used herein, the viscosity of a DVA refers to the viscosity determined by Laboratory Capillary Rheometry (LCR) as described in ASTM D3855-08 at 1200 s<sup>-1</sup>, 220°C, using a 30.0 mm die length, 1.0 mm diameter. As used herein, "UV resistance" refers to the ability of a modified composition to resist change in the tensile strength after aging as defined herein of the thermoplastic elastomeric composition with UV exposure, relative to the tensile strength of the modified composition without

aging.

**[0047]** In an embodiment, the tensile strength of the thermoplastic elastomeric composition after aging is greater than the tensile strength of the composition determined prior to said aging. As used in the present specification and claims, "aging" refers to aging the composition according to SAE J1960 or an equivalent thereof at 1875 kJ/m<sup>2</sup> at 340 nm, and the tensile strength is determined according to ASTM D882-02 or an equivalent thereof.

**[0048]** In an embodiment, the elongation at break of the thermoplastic elastomeric composition after aging is greater than the elongation at break of the composition determined prior to said aging, wherein the composition is aged according to SAE J1960 or an equivalent thereof at 1875 kJ/m<sup>2</sup> at 340 nm. As used in the specification and claims, the elongation at break is determined according to ASTM D882-02 or an equivalent thereof.

**[0049]** Accordingly, the invention provides the following embodiments:

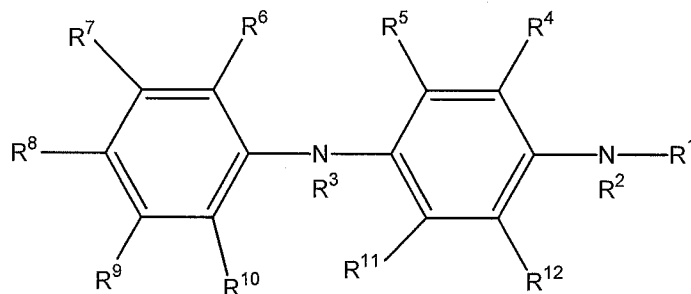
- A. A thermoplastic elastomer composition, comprising a post-vulcanized dynamically vulcanized alloy and a low molecular weight aromatic amine stabilizer, wherein the dynamically vulcanized alloy comprises an isobutylene elastomeric component dispersed as a domain in a continuous phase comprising at least one thermoplastic resin.
- B. A process to produce a thermoplastic elastomer composition, comprising post-vulcanization mixing of a dynamically vulcanized alloy, with a low molecular weight aromatic amine stabilizer, wherein the dynamically vulcanized alloy comprises an isobutylene elastomeric component dispersed as a domain in a continuous phase comprising at least one thermoplastic resin.

- C. A process to produce a thermoplastic elastomer composition, comprising dynamically vulcanizing an isobutylene elastomeric component dispersed as a domain in a continuous phase comprising at least one thermoplastic resin to produce a post-vulcanization dynamically vulcanized alloy; and post-vulcanization mixing of the dynamically vulcanized alloy with a low molecular weight aromatic amine stabilizer to produce the thermoplastic elastomer composition.
- D. A thermoplastic elastomer composition prepared by a process comprising: dynamically vulcanizing a halogenated isobutylene elastomeric component, the elastomeric component comprising not more than 10 phr of a curative or cross-linking agent, dispersed as a domain in a continuous phase comprising a polyamide to produce a post-vulcanization dynamically vulcanized alloy; and post-vulcanization mixing of the dynamically vulcanized alloy with a low molecular weight aromatic amine stabilizer to produce the thermoplastic elastomer composition.
- E. A method to reduce the viscosity and improve the UV resistance of a dynamically vulcanized alloy, comprising: post-vulcanization mixing of the dynamically vulcanized alloy, with a low molecular weight aromatic amine stabilizer to produce a stabilized composition, wherein the dynamically vulcanized alloy comprises an isobutylene elastomeric component dispersed as a domain in a continuous phase comprising a polyamide.
- F. The invention of any one of embodiments A to E, wherein the tensile strength of the composition after aging is greater than the tensile

strength of the composition determined prior to said aging.

- G. The invention of any one of embodiments A to F, wherein the elongation at break of the composition after aging is greater than the elongation at break of the composition determined prior to said aging.
- H. The invention of any one of embodiments A to G, wherein the isobutylene elastomeric component is halogenated.
- I. The invention of any one of embodiments A to H, wherein the isobutylene elastomer comprises from 95 to 25 parts by weight of the composition and the polyamide comprises from 5 to 75 parts by weight of the composition, wherein the total parts by weight of the halogenated isobutylene elastomer and the polyamide totals 100.
- J. The invention of any one of embodiments A to I, wherein the stabilizer is present in the composition at greater than or equal to 1.5 phr.
- K. The invention of any one of embodiment A to J, wherein the stabilizer is present in the composition at not more than 20 or 10 phr or 8 phr.
- L. The invention of any one of embodiments A to K, wherein the isobutylene elastomeric component comprises brominated poly(isobutylene-co-p-methylstyrene).
- M. The invention of any one of embodiments A to L, wherein the polyamide is at least one member selected from the group consisting of Nylon 6, Nylon 66, Nylon 11, Nylon 69, Nylon 12, Nylon 610, Nylon 612, Nylon 48, Nylon MXD6, Nylon 6/66 and copolymers thereof.
- N. The invention of any one of embodiments A to M,

wherein the low molecular weight aromatic amine stabilizer has the general formula:



wherein R<sup>1</sup> is a C<sub>1</sub> to C<sub>20</sub> hydrocarbyl group and R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, R<sup>11</sup>, and R<sup>12</sup> are individually selected from H or C<sub>1</sub>-C<sub>20</sub> hydrocarbyl groups.

- O. The invention of embodiment N wherein any one of R<sup>2</sup> to R<sup>12</sup> is individually selected from H or C<sub>1</sub>-C<sub>10</sub> hydrocarbyl groups.
- P. The invention of any one of embodiments A to O, wherein the low molecular weight aromatic amine stabilizer as a molecular weight of less than or equal to about 500 g/mol.
- Q. The invention of any one of embodiments A to P, wherein the low molecular weight aromatic amine stabilizer comprises a diaryl-p-phenylene diamine.
- R. The invention of any one of embodiments A to Q, wherein the low molecular weight aromatic amine stabilizer is N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine.
- S. The invention of any one of embodiments A to R, wherein the composition further comprises carbon black, a fatty acid, a wax, an antioxidant, a curative, calcium carbonate, clay, silica, a UV absorber, an antiozonant, a tackifier, ZnO, CuI, a scorch inhibiting agent, or a combination thereof.

#### EXAMPLES

[0050] A series of exemplary and comparative compositions were prepared by heating a post-

vulcanization dynamically vulcanized alloy (DVA) while mixing to partially melt the material, followed by adding the stabilizer and other components to the melt while mixing to produce the composition. The compositions were prepared using the materials listed in Table 1.

**Table 1. Component Description**

Trade Name	Description	Supplier
Raven 7000	Carbon black	Columbian Chemicals
Vulcan 9A32	Carbon black	Cabot Corp.
Hombitec RM230L	TiO <sub>2</sub>	Sachtleben
Santoflex 6PPD	N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine Stabilizer	Flexsys
Exxcore DVA,	DVA	Exxonmobil Chemical Company, USA.
ZnO	ZnO	Horsehead Corp.
Durazone 37	Antioxidant/antiozonant	Chemtura
Polystay K	Phenolic antioxidant	Goodyear Chemical
Chimmasorb 119	Hindered amine UV stabilizer	Chembridge Intl. Corp.
UV-3529	Hindered amine UV stabilizer	Dannier Chemical, Inc.
UV-3346	Hindered amine UV stabilizer	Cytec
Tinuvin 622	Hindered amine UV stabilizer	Ciba
UV-2908	Hindered hydroxybenzoate UV stabilizer	Hanson Group
Polystay 100	Diaryl-p-phenylenediamine stabilizer	Goodyear Chemical
Wingstay L	Poly-phenolic antioxidant	Eliokem
Wingstay 29	Antioxidant para oriented styrenated diphenylamines	Eliokem
Zinc stearate	Zinc stearate	Lab stock
Stearic acid	Stearic acid	Lab stock
Nylon 6,66	Nylon 6,66	Exxonmobil
Uniplex 214	N-butylbenzene sulfonamide plasticizer	Unitex
Copper iodide	Copper iodide	Lab stock
Irganox 1098	Antioxidant hindered phenol	Ciba-BASF
Talc	Talc	Lab stock
HPR AR 201	Maleic anhydride-graft-modified ethylene-ethyl acrylate copolymer resin compatibilizer	Mitsui-Dupont
Exxpro 89-4	Halogenated poly(isobutylene-co-p-methylstyrene)	ExxonMobil

[0051] The compositions were tested according to the testing parameters of the methods listed in Table 2.

**Table 2. Test Methods**

Specific Gravity	ASTM-D792	Samples press cured, 5 minutes @ 207°C, 2 mm thickness at 5 seconds
Hardness Shore A, Shore D	ASTM D2240	
10% Modulus (MPa)	ISO-37 ASTM-D412	
50% Modulus (MPa)	ISO-37 ASTM-D412	
100% Modulus (MPa)	ISO-37 ASTM-D412	
Ultimate Tensile Strength (UTS) (MPa)	ISO-37 ASTM-D412	
Ultimate Elongation (%)	ISO-37 ASTM-D412	
Maximum Strain (%)	ISO-37 ASTM-D412	
Weight Gain (%)	TPE-0018	
Laboratory Capillary Rheometry (LCR) (Pa-s)	ASTM D3855	Pa-s @ 1200; 220°C, 30.0 mm die length, 1.0 mm diameter
Tension Set (%)	TPE-0053 ASTM D412	
Tensile Strength (psi)	ISO 37 British Std	
Elongation at break (%)	ISO 37 British Std	
Aging	SAE J1960	1875 kJ/m <sup>2</sup> @ 340 nm

**[0052]** A series of six compositions were prepared by first forming the DVA to produce a post-vulcanization DVA, and then melt mixing the DVA with or without the selected low molecular weight amine stabilizer. The results are listed in Table 3 below. The compositions obtained were then prepared and tested. The test results are shown in Table 4.



**Table 3. Test Compositions**

Component	Comp. 1 (phr)	Comp. 2 (phr)	Comp. 3 (phr)	Comp. 4 (phr)	Comp. 5 (phr)	Comp. 6 (phr)
Exxpro	100.00	100.00	100.00	100.00	100.00	100.00
Talc	2.50	2.50	2.50	2.50	2.50	2.50
ZnO	0.15	0.15	0.15	0.15	0.15	0.15
Zinc Stearate	0.30	0.30	0.30	0.30	0.30	0.30
Stearic Acid	0.65	0.65	0.65	0.65	0.65	0.65
Nylon 6,66	62.97	62.97	62.97	62.97	62.97	62.97
Uniplex 214	26.99	26.99	26.99	26.99	26.99	26.99
Copper Iodide	0.03	0.03	0.03	0.03	0.03	0.03
Irganox 1098	0.32	0.32	0.32	0.32	0.32	0.32
Tinuvin 622LD	0.13	0.13	0.13	0.13	0.13	0.13
AR201	10.05	10.05	10.05	10.05	10.05	10.05
DVA Total	204.08	204.08	204.08	204.08	204.08	204.08
6PPD	0	0.5	1	2	4	8
Total	204.08	204.58	205.08	206.08	208.08	212.08
6PPD (wt%)	0	0.24%	0.49%	0.98%	1.96%	3.92%
Torque at Dump (m-g)	1850	1260	1250	1230	1240	1210
Melt Temp (°C)	213	211	213	212	212	210
Batch Time (min)	3	3	3	3	3	3

**Table 4. Test Results**

Test	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	Comp. 6
Specific Gravity	1.023	10.24	1.023	1.023	1.011	1.003
Hardness, 5 sec Shore A	86	84	85	86	86	83
Hardness, 5 sec Shore D	28	27	28	28	29	28
10% Modulus (MPa)	2.65	3.39	3.28	3.39	3.75	3.74
50% Modulus (MPa)	6.54	6.89	6.44	6.48	7.03	6.8
100% Modulus (MPa)	9.41	9.90	9.08	9.04	9.77	9.34
UTS (MPa)	10.95	13.80	13.60	13.88	15.85	17.49
Ultimate Elongation (%)	117	188	199	206	221	282
Maximum Strain (%)	148	213	224	234	243	304
Weight Gain (%)	46	33	38	35	34	36
LCR (Pa-s)	377	443	401	361	322	275
Tension Set (%)	32	38	37	34	36	37

**[0053]** As seen in Tables 3 and 4, the melt viscosity as indicated by the torque at dump is lowered in

proportion to the amount of amine stabilizer (6PPD) added; however, quite surprisingly, the UV stabilization as reflected in the tension set data is about the same and not significantly different regardless of the amount of stabilizer. This indicates that the amine stabilizer can effect UV stabilization while simultaneously using the amount of stabilizer added post-vulcanization to control the desired melt viscosity of the composition.

**[0054]** In another set of examples, the DVA utilized in Composition 1 was post-vulcanization melt blended with various samples of carbon black and  $\text{TiO}_2$  without amine stabilizer for comparison, and with 2.5 phr of the low molecular weight amine stabilizer (6PPD) to produce the inventive compositions. The LCR, tensile strength, and elongation at break of each composition were measured. The compositions were subjected to aging, and the tensile strength re-measured to determine the change in tensile strength after aging. The data are shown in Table 5.

**Table 5. Compounded Formulations Aging Testing**

Composition	Carbon Black (1.5 phr)	TiO <sub>2</sub> (1.5 phr)	6PPD (phr)	LCR (Pa-s)	Tensile Strength (MPa)	Elongation at break (%)	Aged tensile strength (% change)
Comp. 7				742	11.89	289	-69.5
Comp. 8	Raven 7000			749	12.67	344	-7.35
Comp. 9	Vulcan 9a32			721	12.98	312	-2.14
Comp. 10		RM230L		741	12.53	320	-53.14
Comp. 11	Raven 7000	RM230L		791	9.928	220	1.51
Comp. 12	Vulcan 9a32	RM230L		774	12.13	324	-4.66
Comp. 13	Raven 7000	RM300		739	11.91	314	-1.56
Comp. 14		RM300		752	12.09	298	-46.62
Comp. 15	Vulcan 9a32	RM300		803	12.83	302	-2.71
Comp. 16			2.5	548	16.96	388	-62.61
Comp. 17	Raven 7000		2.5	595	16.37	383	-5.57
Comp. 18	Vulcan 9a32		2.5	593	17.81	395	-1.55
Comp. 19		RM230L	2.5	601	16.50	381	-49.33
Comp. 20	Raven 7000	RM230L	2.5	602	16.68	382	-1.46
Comp. 21	Vulcan 9a32	RM230L	2.5	635	16.51	351	9.12
Comp. 22		RM300	2.5	561	15.55	377	-49.50
Comp. 23	Raven 7000	RM300	2.5	630	10.53	228	5.06
Comp. 24	Vulcan 9a32	RM300	2.5	602	16.97	393	-6.58

**[0055]** The data in Table 5 show that the presence of the amine stabilizer reduced the viscosity of compositions prepared with carbon black and/or TiO<sub>2</sub>, as seen in the lowered LCR data of compositions 16 to 24 relative to compositions 7 to 15 without the amine stabilizer. The amine stabilizer also improved (increased) the tensile strength and elongation at break, and also generally resulted in less decrease or a greater increase in the aged tensile strength.

**[0056]** Examples were prepared by melt mixing the post-vulcanized DVA utilized in Composition 1 with a variety of components typical of an end use in a pneumatic tire application. The compositions were prepared with carbon black, zinc oxide and with and without various

stabilizers and antioxidants. The tensile strength and elongation were measured, the samples aged and the tensile strength and elongation were again measured to determine the change in tensile strength and the change in elongation at break after aging. The results are shown in Tables 6, 7, and 8.

**Table 6. Compositions 25 to 34**

Component / Property	Comp. 25 (phr)	Comp. 26 (phr)	Comp. 27 (phr)	Comp. 28 (phr)	Comp. 29 (phr)	Comp. 30 (phr)	Comp. 31 (phr)	Comp. 32 (phr)	Comp. 33 (phr)	Comp. 34 (phr)
DVA	204.03	204.03	204.03	204.03	204.03	204.03	204.03	204.03	204.03	204.03
Carbon black		0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	
ZnO 20		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Durazone 37						1.5	3.0			
Polystay K				1.5	3.0					
Chinmasorb 119		1.5	3.0							
6PPD							1.5	3.0		
Tensile Strength (% change)	100	11.0	8.0	32.7	27.2	24.6	3.1	32.2	13.4	100
Elongation at break (% change)	100	48.8	58.7	69.1	61.5	42.0	6.8	54.6	10.5	100

**Table 7. Compositions 35 to 44**

Component	Comp. 35 (phr)	Comp. 36 (phr)	Comp. 37 (phr)	Comp. 38 (phr)	Comp. 39 (phr)	Comp. 40 (phr)	Comp. 41 (phr)	Comp. 42 (phr)	Comp. 43 (phr)	Comp. 44 (phr)
DVA	204.03	204.03	204.03	204.03	204.03	204.03	204.03	204.03	204.03	204.03
Carbon black	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
ZnO K-911	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
UV 3529					1.5	3.0				
UV 3346			1.5	3.0						
Tinuvin 622	1.5	3.0								
UV 2908							1.5	3.0		
Polystay 100									1.5	3.0
Tensile Strength (% change)	-1	19.2	42.2	27.3	5.7	8.2	28.5	20.4	-29.4	6.0
Elongation at break (% change)	45.8	31.4	64.4	66.3	58.1	42.5	75.7	41.4	4.4	22.2

**Table 8. Compositions 45 to 50**

Component	Comp. 45 (phr)	Comp. 46 (phr)	Comp. 47 (phr)	Comp. 48 (phr)	Comp. 49 (phr)	Comp. 50 (phr)
DVA	204.03	204.03	204.03	204.03	204.03	204.03
Carbon black	0.75	0.75	0.75	0.75	0.75	0.75
ZnO K-911	1.5	1.5	1.5	1.5	1.5	1.5
Polystay 100					1.5	3.0
Wingstay L			1.5	3.0		
Wingstay 29	1.5	3.0				
Tensile Strength (% change)	2.1	18.3	27.2	-3.3	3.3	-4.5
Elongation at break (% change)	54.9	42.3	59.4	89.8	11.3	-3.3

**[0057]** Accordingly, as the data show, the post-vulcanization mixing of a low molecular weight stabilizer in a DVA results in a composition having improved processability including a reduced viscosity and improved UV resistance, especially in the case of the inventive low molecular weight amine stabilizers in compositions 31, 32 and 43-50.

**[0058]** Any range of numbers recited in the specification hereinabove or in the claims hereinafter, such as that representing a particular set of properties, units of measure, conditions, physical states or percentages, is intended to literally incorporate expressly herein by reference or otherwise, any number falling within such range, including any subset of numbers or ranges subsumed within any range so recited.

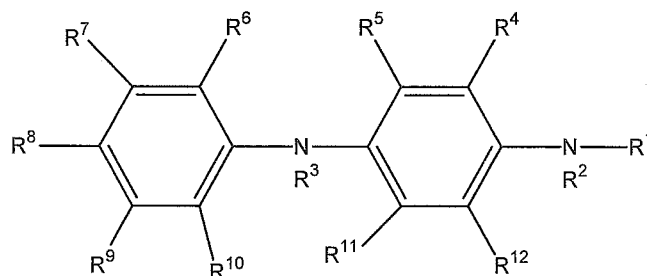
**[0059]** All documents described herein are incorporated by reference herein, including any patent applications and/or testing procedures to the extent that they are not inconsistent with this application and claims. The principles, preferred embodiments, and modes of operation of the present invention have been described in the foregoing specification. Although the invention herein has been described with reference to particular embodiments, it is to be understood that these embodiments are merely illustrative of the principles and applications of the present invention. It is therefore to be understood that numerous modifications may be made

to the illustrative embodiments and that other arrangements may be devised without departing from the spirit and scope of the present invention as defined by the appended claims.

CLAIMS:

We Claim:

1. A process to produce a thermoplastic elastomer composition, comprising:  
dynamically vulcanizing an isobutylene elastomeric component dispersed as a domain in a continuous phase comprising at least one thermoplastic resin to produce a post-vulcanized dynamically vulcanized alloy; and  
mixing of the post-vulcanized dynamically vulcanized alloy with a low molecular weight aromatic amine stabilizer to produce the thermoplastic elastomer composition.
2. The process of claim 1, wherein the tensile strength of the composition after aging is greater than the tensile strength of the composition determined prior to said aging, or wherein the elongation at break of the composition after aging is greater than the elongation at break of the composition determined prior to said aging.
3. The process of claim 1 or 2, wherein the isobutylene elastomeric component comprises from 95 to 25 parts by weight, and the thermoplastic resin comprises from 5 to 75 parts by weight, wherein the total parts by weight of the isobutylene elastomeric component and the thermoplastic resin totals 100.
4. The process of any one of claims 1 to 3, wherein the stabilizer is present at greater than or equal to 1.5 phr.
5. The process of any one of claims 1 to 4, wherein the low molecular weight aromatic amine stabilizer has the general formula:



wherein  $R_1$  is a  $C_1$  to  $C_{20}$  hydrocarbyl group and  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$ , and  $R^{12}$  are individually H or  $C_1$ - $C_{20}$  hydrocarbyl groups.

6. The process of any one of claims 1 to 5, wherein the low molecular weight aromatic amine stabilizer has a molecular weight of less than or equal to 500 g/mol.

7. The process of any one of claims 1 to 6, wherein the low molecular weight aromatic amine stabilizer comprises a diaryl-p-phenylene diamine.

8. The process of any one of claims 1 to 6, wherein the low molecular weight aromatic amine stabilizer comprises N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine.

9. The process of any one of claims 1 to 8, wherein the at least one thermoplastic resin is at least one polyamide selected from the group consisting of Nylon 6, Nylon 66, Nylon 11, Nylon 69, Nylon 12, Nylon 610, Nylon 612, Nylon 48, Nylon MXD6, Nylon 6/66 and copolymers thereof.

10. A thermoplastic elastomer composition, comprising a post-vulcanized dynamically vulcanized alloy and a low molecular weight aromatic amine stabilizer, wherein the dynamically vulcanized alloy comprises an isobutylene elastomeric component dispersed as a domain in a continuous phase comprising at least one thermoplastic resin.

11. The composition of claim 10, wherein the isobutylene elastomeric component comprises from 95 to 25 parts by weight and the thermoplastic resin comprises from 5 to 75 parts by weight, wherein the total parts by weight of the isobutylene elastomeric component and the thermoplastic resin totals 100.

12. The composition of claim 10 or 11, wherein the stabilizer is present at greater than or equal to 1.5 phr.

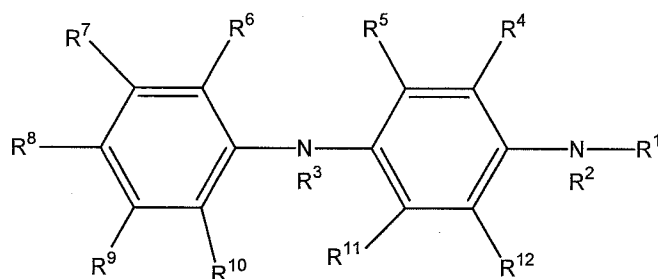
13. The composition of any one of claims 10 to 12,



wherein the isobutylene elastomeric component comprises brominated poly(isobutylene-co-p-methylstyrene).

14. The composition of any one of claims 10 to 13, wherein the thermoplastic resin is at least one polyamide selected from the group consisting of Nylon 6, Nylon 66, Nylon 11, Nylon 69, Nylon 12, Nylon 610, Nylon 612, Nylon 48, Nylon MXD6, Nylon 6/66 and copolymers thereof.

15. The composition of any one of claims 10 to 14, wherein the low molecular weight aromatic amine stabilizer has the general formula:



wherein R<sup>1</sup> is a C<sub>1</sub> to C<sub>20</sub> hydrocarbyl group and R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, R<sup>11</sup>, and R<sup>12</sup> are individually H or C<sub>1</sub>-C<sub>10</sub> hydrocarbyl groups.

16. The composition of any one of claims 10 to 15, wherein the low molecular weight aromatic amine stabilizer has a molecular weight of less than or equal to 500 g/mol.

17. The composition of any one of claims 10 to 16, wherein the low molecular weight aromatic amine stabilizer comprises a diaryl-p-phenylene diamine.

18. The composition of any one of claims 10 to 16, wherein the low molecular weight aromatic amine stabilizer is N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine.

19. The composition of any one of claims 10 to 18, further comprising carbon black, a fatty acid, a wax, an antioxidant, a curative, calcium carbonate, clay, silica, a UV absorber, an antiozonant, a tackifier, ZnO, CuI, a scorch inhibiting agent, or a combination thereof.

20. A thermoplastic elastomer composition prepared by a process comprising:

dynamically vulcanizing a halogenated isobutylene elastomeric component, wherein the elastomeric component is blended with not more than 10 phr of a cross-linking agent, dispersed as a domain in a continuous phase comprising a polyamide to produce a post-vulcanized dynamically vulcanized alloy; and

mixing of the post-vulcanized dynamically vulcanized alloy with 1.5 to 10 phr of a low molecular weight aromatic diamine stabilizer to produce the thermoplastic elastomer composition.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/43134

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3. ☒ Claims Nos.: 4-9 and 13-19  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/43134

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C08L 9/00 (2012.01)

USPC - 525/98, 525/99, 525/191, 525/192

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)

IPC(8) - C08L 9/00 (2012.01)

USPC - 525/98, 525/99, 525/191, 525/192

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
Patents. Non-Patent Literature. Search Term limited. USPC - 525/99, 525/191, 525/192

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

PubWEST (PGPB, USPT, EPAB, JPAB): Search Term Limited - see extra sheet

Google Patents: isobutylene elastomeric component dynamic vulcanization (About 350 results)

Google Scholar: dynamic vulcanization thermoplastic elastomer (About 9240 results)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2009/0312458 A1 (Stevenson et al.) 17 December 2009 (17.12.2009); para [0001], [0008], [0016], [0020], [0021], [0025], [0046], [0029], [0034], [0049], [0050], [0066], [0067].	1-3, 10-12 and 20
Y	US 5,849,820 A (Kim et al.) 15 December 1998 (15.12.1998); col. 1, ln. 5-8; col. 2, ln. 36-41, 43-48; col. 5, ln. 43-51, 52, 56-57; col. 6, ln. 10-11, 21-23, 27-29, 29-31, 31-33, 39-41; col. 14, ln. 1-50.	1-3, 10-12 and 20
Y	US 6,825,277 B2 (van Issum et al.) 30 November 2004 (30.11.2004); col. 1, ln. 6-12; col. 3, ln. 66 to col. 4, ln. 2; col. 4, ln. 10-20, 38-39; col. 6, ln. 5-9, 22-32, 31-36; col. 8, ln. 9-24, 21-24; col. 9, ln. 23-30, 31-36, 42-43, 45-49; col. 10, ln. 7-11; col. 11, ln. 15, 20-21, 27-32; col. 12, ln. 19-32, 23-32, 26, 29-30.	1-3, 10-12 and 20
Y	US 2008/0314492 A1 (Tsou et al.) 25 December 2008 (28.12.2008) especially abstract; para [0008]-[0044]	1-3, 10-12 and 20

☐ Further documents are listed in the continuation of Box C.

\* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

16 August 2012 (16.08.2012)

Date of mailing of the international search report

12 SEP 2012

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/43134

Search Terms: process, method, thermoplastic elastomer, isobutylene elastomer, component, thermoplastic resin, polyamide, nylon, DVA, dynamically vulcanized alloy, dynamic vulcanization, dynamically vulcanized, amine, stabilizer, amine thermal stabilizer, amine stabilizer, aromatic amine stabilizer, N,N-diphenyl-N-phenyl-p-phenylenediamine, tensile strength, additive, N-(1,3-dimethylbutyl)-N-phenyl-p-phenylenediamine, poly(isobutylene-co-p-methylstyrene), isobutylene, post-aging, post vulcanization, phenylenediamine, phenylene diamine, UV, ultraviolet, thermal, elongation, alkyl, aryl, Sato Shun, Hana Yuichi, Blok Edward, Ellul Maria, Dias Anthony, Randall Kerkestetter Howard, The Yokohama Rubber Co., Exxonmobil.