(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 July 2017 (27.07.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/127603 A1

(51) **International Patent Classification**:
B60C 1/00 (2006.01) ***C08L 1/10*** (2006.01)
C08F 291/02 (2006.01) ***C08L 1/12*** (2006.01)
C08J 5/00 (2006.01)

(21) **International Application Number**:
PCT/US2017/014223

(22) **International Filing Date**:
20 January 2017 (20.01.2017)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
62/281,208 21 January 2016 (21.01.2016) US
15/409,644 19 January 2017 (19.01.2017) US

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(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, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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, ST, 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, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

WO 2017/127603 A1

(54) **Title**: ELASTOMERIC COMPOSITIONS COMPRISING CELLULOSE ESTER ADDITIVES

(57) **Abstract**: An elastomeric composition is provided comprising at least one elastomer, at least one cellulose ester additive, at least one methylene acceptor, at least one methylene donor, and optionally, at least one filler; wherein the cellulose ester additive comprises at least one cellulose ester. The cellulose ester additive can also comprise at least one compatibilizer and/or plasticizer.

Elastomeric Compositions Comprising Cellulose Ester Additives

Conventionally, in order to produce elastomeric compositions with increased stiffness and tear resistance, large quantities of additives such as fillers (e.g., carbon black, silica, and other minerals), sulfur and vulcanization accelerators have been incorporated. Phenolic resin is also widely used in order to further increase the stiffness of the rubber composition. These solutions can often bring additional problems like processability issues due to high viscosity, blooming of sulfur, safety hazards, and increased cost. For example, fillers can cause processing viscosity and hysteresis to increase, rolling resistance to increase, and higher heat built-up. The addition of sulfur can reduce scorch time and cause blooming. It has been found that phenolic resins are expensive and can cause safety hazards due to the release of formaldehyde, volatile side products, and ammonia gas plus can reduce the strength at break of elastomeric compositions.

There is a need in the industry to overcome these disadvantages by selecting an additive that improves processing of elastomeric compositions and yet increases stiffness and tear resistance.

The use of cellulose ester additives (CEA) in an elastomeric composition containing methylene acceptors and methylene donors is found to have improved stiffness, tear resistance, and better processability. In addition, stiffness can be improved by about 10% to about 50%, and tear resistance can be improved by about 30% to about 200% with better processability. In the meantime, other physical properties and performance are retained without significant deterioration. The CEA can be added in tire components where a methylene acceptor is used, for instance, in apex, tread, sidewall, bead, skim, carcass, sidewall insert compounds. The CEA can further be used in applications besides tires.

This invention relates generally to the dispersion of a cellulose ester additive (CEA) into elastomeric compositions containing a methylene acceptor and donor in order to improve the mechanical and physical properties of the

elastomeric composition. It has been observed that CEA can provide a dual functionality when utilized in elastomeric compositions and their production. This technology can be used to produce tires with improved steerability/handling stability and tear resistance along with processability. The improvement in elastomeric composition rigidity/hardness/stiffness can result in a thinner tire component leading to material costs reduction, and lighter more fuel efficient tires. Further, the CEA can facilitate commonly known processing methodologies using internal mixers, extruders, calendars and mills used in making these components by positively affecting formulation viscosity, mixing time/quality and filler dispersion and thereby increasing productivity and reducing cost. These improved component properties can be further translated into new tire component designs. The invention is applicable, but not limited to, passenger (PCR), truck/bus (TBR), off-the-road (OTR), and aircraft tire applications. The CEA can further be used in applications besides tires.

Summary of the Invention

In one embodiment of the invention, an elastomeric composition is provided comprising at least one elastomer, at least one cellulose ester additive, at least one methylene acceptor, at least one methylene donor, and optionally, at least one filler compound. In another embodiment of the invention, a process to produce an elastomeric composition is provided comprising mixing at least one elastomer, at least one cellulose ester additive, at least one methylene acceptor, at least one methylene donor, and optionally, at least one filler compound. In another embodiment of the invention, a tire comprising an elastomeric composition is provided, wherein the elastomeric composition comprises at least one elastomer, at least one cellulose ester additive, at least one methylene acceptor, at least one methylene donor, and optionally, at least one filler compound. In yet another embodiment of the invention, an article is provided comprising an elastomeric composition, wherein the elastomeric composition comprises at least one elastomer, at least one cellulose ester additive, at least one methylene

acceptor, at least one methylene donor, and optionally, at least one filler compound.

Detailed Description

In one embodiment of the invention, an elastomeric composition is provided comprising at least one elastomer, at least one cellulose ester additive, at least one methylene acceptor, at least one methylene donor, and optionally, at least one filler compound.

The term "elastomer," as used herein, can be used interchangeably with the term "rubber." Due to the wide applicability of the process described herein, the CEA can be employed with virtually any type of elastomer. For instance, the elastomers utilized in this invention can comprise a natural rubber, a modified natural rubber, a synthetic rubber, and mixtures thereof.

The elastomer of the invention may also include one or more rubbers including, but are not limited to, polyisoprene rubber, poly(styrene-co-butadiene) rubber (SBR), polybutadiene rubber (BR), poly(isoprene-co-butadiene) rubber (IBR), styrene-isoprene-butadiene rubber (SIBR), ethylene-propylene rubber (EPM), ethylene-propylene-diene rubber (EPDM), polysulfide, nitrile rubber, propylene oxide polymers, butyl rubber, halogenated butyl rubber, brominated butyl rubber, chlorinated butyl rubber, star-branched polyisobutylene rubber, star-branched brominated butyl (polyisobutylene/isoprene copolymer) rubber; poly(isobutylene-co-p-methylstyrene) and halogenated poly(isobutylene-co-p-methylstyrene), such as, for example, terpolymers of isobutylene derived units, p-methylstyrene derived units, and p-bromomethylstyrene derived units, and mixtures thereof. Common diene rubbers that can be utilized are polymers based on conjugated dienes such as, but not limited to, 1,3-butadiene; 2-methyl-1,3-butadiene; 1,3-pentadiene; 2,3-dimethyl-1,3-butadiene; and the like, as well as copolymers of such conjugated dienes with monomers such as, for example, styrene, alpha-methylstyrene, acetylene, e.g., vinyl acetylene,

acrylonitrile, methacrylonitrile, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, vinyl acetate, and the like.

In one embodiment of the invention, the elastomers are selected from the group consisting of natural rubber, cis-polyisoprene, polybutadiene (including high cis-polybutadiene), or styrene-butadiene copolymers, styrene-isoprene copolymers, isoprene-butadiene copolymers, styrene-isoprene-butadiene tripolymers and like. Moreover, mixtures of two or more elastomers from the aforementioned groups may be utilized in this invention.

In certain embodiments of the present invention, at least one of the elastomers is a non-polar elastomer. For example, a non-polar elastomer can comprise at least about 90, 95, 98, 99, or 99.9 weight percent of non-polar monomers. In one embodiment, the non-polar elastomer is primarily based on a hydrocarbon. Examples of non-polar elastomers include, but are not limited to, natural rubber, polybutadiene rubber, polyisoprene rubber, butyl rubber, styrene-butadiene rubber, polyolefins, ethylene propylene monomer rubber (EPM), ethylene propylene diene monomer (EPDM) rubber, and polynorbornene rubber. Examples of polyolefins include, but are not limited to, polybutylene, polyisobutylene, and ethylene propylene rubber. In another embodiment, the elastomer comprises a natural rubber, a styrene-butadiene rubber, and/or a polybutadiene rubber. Non-polar elastomers are often used in tire components.

In certain embodiments, the elastomer contains little or no nitrile groups. As used herein, the elastomer is considered a “non-nitrile” elastomer when nitrile monomers make up less than 10 weight percent of the elastomer. In one embodiment, the elastomer contains no nitrile groups.

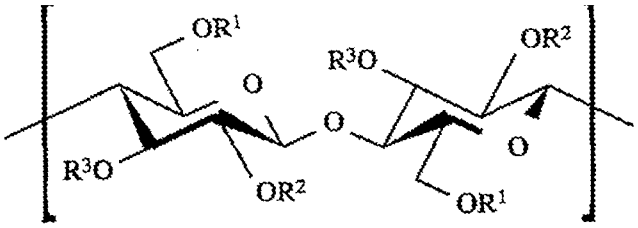
The elastomeric composition of the present invention can comprise at least about 0.5, 1, 2, 3, 4, or 5 parts per hundred rubber (“phr”) of at least one cellulose ester additive, based on the total weight of the elastomers. Additionally or alternatively, the elastomeric composition of the present invention can comprise not more than about 75, 50, 40, 30, 20, 15, 10, or 8 phr of at least one cellulose ester additive, based on the total weight of the

elastomers. The term "phr," as used herein, refers to parts of a respective material per 100 parts by weight of rubber or elastomer. In other embodiments of the invention, the amount of cellulose ester additive in the elastomeric composition can range from about 0.5 to about 40 phr, from about 0.5 to about 20 phr, about 0.5 to about 15 phr, about 1 to about 10, and about 1 to about 8.

The term "cellulose ester" or "cellulose ester additive" can be used interchangeably to mean a cellulose ester or a modified cellulose ester. In one embodiment of the invention, a modified cellulose ester comprises at least one cellulose ester and at least one plasticizer. In another embodiment, a modified cellulose ester comprises at least one cellulose ester and at least one compatibilizer. In yet another embodiment of the invention, a modified cellulose ester comprises at least one cellulose ester, at least one plasticizer, and at least one compatibilizer.

The cellulose esters useful in the present invention can be prepared using techniques known in the art or can be commercially obtained, e.g., from Eastman Chemical Company, Kingsport, TN, U.S.A.

The cellulose esters of the present invention generally comprise repeating units of the structure:



wherein R^1, R^2, and R^3 may be selected independently from the group consisting of hydrogen or a straight chain alkanoyl having from 2 to 10 carbon atoms, wherein at least 5% of R groups are 3-10 carbon atoms. In other embodiments of the invention, at least 10%, at least 20% and at least 30% of the R groups of the cellulose esters have 3-10 carbon atoms. Cellulose esters of this invention do not include cellulose acetate. For cellulose esters, the substitution level is usually expressed in terms of degree of substitution

("DS"), which is the average number of substitutents per anhydroglucose unit ("AGU"). Generally, conventional cellulose contains three hydroxyl groups per AGU that can be substituted; therefore, the DS can have a value between zero and three. Alternatively, lower molecular weight cellulose mixed esters can have a total degree of substitution ranging from about 3.08 to about 3.5. Generally, cellulose is a large polysaccharide with a degree of polymerization from 700 to 2,000 and a maximum DS of 3.0. However, as the degree of polymerization is lowered, as in low molecular weight cellulose mixed esters, the end groups of the polysaccharide backbone become relatively more significant, thereby resulting in a DS ranging from about 3.08 to about 3.5.

Because DS is a statistical mean value, a value of 1 does not assure that every AGU has a single substituent. In some cases, there can be unsubstituted AGUs, some with two substitutents, and some with three substitutents. The "total DS" is defined as the average number of substitutents per AGU. In one embodiment of the invention, the cellulose esters can have a total DS per AGU (DS/AGU) of at least about 0.5, 0.8, 1.2, 1.5, or 1.7. Additionally or alternatively, the cellulose esters can have a total DS/AGU of not more than about 3.0, 2.9, 2.8, or 2.7. The DS/AGU can also refer to a particular substituent, such as, for example, hydroxyl, acetyl, butyryl, or propionyl. For instance, a cellulose acetate propionate ("CAP") and cellulose acetate butyrate ("CAB") can have a total DS/AGU of about 1.7 to about 2.8.

The cellulose ester can be a cellulose triester or a secondary cellulose ester. Examples of cellulose triesters include, but are not limited to, cellulose tripropionate, or cellulose tributyrate. Examples of secondary cellulose esters include cellulose acetate propionate, and cellulose acetate butyrate. These cellulose esters are described in U.S. Patents Nos. 1,698,049; 1,683,347; 1,880,808; 1,880,560; 1,984,147, 2,129,052; and 3,617,201, which are incorporated herein by reference in their entirety to the extent they do not contradict the statements herein.

In one embodiment of the invention, the cellulose ester is selected from the group consisting of cellulose acetate propionate, cellulose acetate butyrate, cellulose tripropionate, cellulose tributyrate, and mixtures thereof.

The degree of polymerization ("DP") as used herein refers to the number of AGUs per molecule of cellulose ester. In one embodiment of the invention, the cellulose esters can have a DP of at least about 2, 10, 50, or 100. Additionally or alternatively, the cellulose esters can have a DP of not more than about 10,000, 8,000, 6,000, or 5,000.

In certain embodiments, the cellulose esters can have an inherent viscosity ("IV") of at least about 0.2, 0.4, 0.6, 0.8, or 1.0 deciliters/gram as measured at a temperature of 25°C for a 0.25 gram sample in 100 ml of a 60/40 by weight solution of phenol/tetrachloroethane. Additionally or alternatively, the cellulose esters can have an IV of not more than about 3.0, 2.5, 2.0, or 1.5 deciliters/gram as measured at a temperature of 25°C for a 0.25 gram sample in 100 ml of a 60/40 by weight solution of phenol/tetrachloroethane.

In certain embodiments, the cellulose esters can have a falling ball viscosity of at least about 0.005, 0.01, 0.05, 0.1, 0.5, 1, or 5 pascals-second ("Pa·s"). Additionally or alternatively, the cellulose esters can have a falling ball viscosity of not more than about 50, 45, 40, 35, 30, 25, 20, or 10 Pa·s.

In certain embodiments, the cellulose esters can have a hydroxyl content of at least about 1.2, 1.4, 1.6, 1.8, or 2.0 weight percent.

In certain embodiments, the cellulose esters useful in the present invention can have a weight average molecular weight (M_w) of at least about 5,000, 10,000, 15,000, or 20,000 as measured by gel permeation chromatography ("GPC"). Additionally or alternatively, the cellulose esters useful in the present invention can have a weight average molecular weight (M_w) of not more than about 400,000, 300,000, 250,000, 100,000, or 80,000 as measured by GPC. In another embodiment, the cellulose esters useful in the present invention can have a number average molecular weight (M_n) of at least about 2,000, 4,000, 6,000, or 8,000 as measured by GPC. Additionally

or alternatively, the cellulose esters useful in the present invention can have a number average molecular weight (M_n) of not more than about 100,000, 80,000, 60,000, or 40,000 as measured by GPC.

In certain embodiments, the cellulose esters can have a glass transition temperature ("Tg") of at least about 50℃, 55℃, 60℃, 65℃, 70℃, 75℃, or 80℃. Additionally or alternatively, the cellulose esters can have a Tg of not more than about 170℃, 160℃, 150℃, 140℃, or 130℃. In contrast, cellulose acetate is not utilized in this invention since it has a Tg of between 180-190℃ and has been found not to disperse well in elastomeric formulations.

In one embodiment of the present invention, the cellulose esters utilized in the elastomeric composition compositions have not previously been subjected to fibrillation or any other fiber-producing process. In such an embodiment, the cellulose esters are not in the form of fibrils and can be referred to as "non-fibril."

The cellulose esters can be produced by any method known in the art. Examples of processes for producing cellulose esters are taught in Kirk-Othmer, Encyclopedia of Chemical Technology, 5th Edition, Vol. 5, Wiley-Interscience, New York (2004), pp. 394-444. Cellulose, the starting material for producing cellulose esters, can be obtained in different grades and from sources such as, for example, cotton linters, softwood pulp, hardwood pulp, corn fiber and other agricultural sources, and bacterial celluloses.

One method of producing cellulose esters is by esterification. In such a method, the cellulose is mixed with the appropriate organic acids, acid anhydrides, and catalysts and then converted to a cellulose triester. Ester hydrolysis is then performed by adding a water-acid mixture to the cellulose triester, which can be filtered to remove any gel particles or fibers. Water is added to the mixture to precipitate out the cellulose ester. The cellulose ester can be washed with water to remove reaction by-products followed by dewatering and drying.

The cellulose triesters that are hydrolyzed can have three substitutents selected independently from alkanoyls having from 2 to 10 carbon atoms. Examples of cellulose triesters include cellulose tripropionate, and cellulose tributyrate or mixed triesters of cellulose such as cellulose acetate propionate and cellulose acetate butyrate. These cellulose triesters can be prepared by a number of methods known to those skilled in the art. For example, cellulose triesters can be prepared by heterogeneous acylation of cellulose in a mixture of carboxylic acid and anhydride in the presence of a catalyst such as H_2SO_4. Cellulose triesters can also be prepared by the homogeneous acylation of cellulose dissolved in an appropriate solvent such as LiCl/DMAc or LiCl/NMP.

After esterification of the cellulose to the triester, part of the acyl substitutents can be removed by hydrolysis or by alcoholysis to give a secondary cellulose ester. Secondary cellulose esters can also be prepared directly with no hydrolysis by using a limiting amount of acylating reagent. This process is particularly useful when the reaction is conducted in a solvent that will dissolve cellulose.

In another embodiment of the invention, low molecular weight mixed cellulose esters can be utilized, such as those disclosed in U.S. Patent No. 7,585,905, which is incorporated herein by reference to the extent it does not contradict the statements herein.

In one embodiment of the invention, a low molecular weight mixed cellulose ester is utilized that has the following properties: (A) a total DS/AGU of from about 3.08 to about 3.50 with the following substitutions: a DS/AGU of hydroxyl of not more than about 0.70, a DS/AGU of C3/C4 esters from about 0.80 to about 1.40, and a DS/AGU of acetyl of from about 1.20 to about 2.34; an IV of from about 0.05 to about 0.15 dL/g, as measured in a 60/40 (wt./wt.) solution of phenol/tetrachloroethane at 25°C; a number average molecular weight of from about 1,000 to about 5,600; a weight average molecular weight of from about 1,500 to about 10,000; and a polydispersity of from about 1.2 to about 3.5.

In another embodiment of the invention, a low molecular weight mixed cellulose ester is utilized that has the following properties: a total DS/AGU of from about 3.08 to about 3.50 with the following substitutions: a DS/AGU of hydroxyl of not more than about 0.70; a DS/AGU of C3/C4 esters from about 1.40 to about 2.45, and DS/AGU of acetyl of from about 0.20 to about 0.80; an IV of from about 0.05 to about 0.15 dL/g, as measured in a 60/40 (wt./wt.) solution of phenol/tetrachloroethane at 25°C; a number average molecular weight of from about 1,000 to about 5,600; a weight average molecular weight of from about 1,500 to about 10,000; and a polydispersity of from about 1.2 to about 3.5.

In yet another embodiment of the invention, a low molecular weight mixed cellulose ester is utilized that has the following properties: a total DS/AGU of from about 3.08 to about 3.50with the following substitutions: a DS/AGU of hydroxyl of not more than about 0.70; a DS/AGU of C3/C4 esters from about 2.11 to about 2.91, and a DS/AGU of acetyl of from about 0.10 to about 0.50; an IV of from about 0.05 to about 0.15 dL/g, as measured in a 60/40 (wt./wt.) solution of phenol/tetrachloroethane at 25°C; a number average molecular weight of from about 1,000 to about 5,600; a weight average molecular weight of from about 1,500 to about 10,000; and a polydispersity of from about 1.2 to about 3.5.

The cellulose ester additive can be modified by the addition of a plasticizer and/or compatibilizer. The plasticizer utilized in this invention can be any that is known in the art that can reduce the melt temperature and/or the melt viscosity of the cellulose ester. The plasticizer can be either monomeric or polymeric in structure. In one embodiment, the plasticizer is at least one selected from the group consisting of a phosphate plasticizer, benzoate plasticizer, adipate plasticizer, a phthalate plasticizer, a glycolic acid ester, a citric acid ester plasticizer and a hydroxyl-functional plasticizer.

In one embodiment of the invention, the plasticizer can be selected from at least one of the following: triphenyl phosphate, tricresyl phosphate, cresyldiphenyl phosphate, octyldiphenyl phosphate, diphenylbiphenyl

phosphate, trioctyl phosphate, tributyl phosphate, diethyl phthalate, dimethoxyethyl phthalate, dimethyl phthalate, dioctyl phthalate, dibutyl phthalate, di-2-ethylhexyl phthalate, butylbenzyl phthalate, dibenzyl phthalate, butyl phthalyl butyl glycolate, ethyl phthalyl ethyl glycolate, methyl phthalyl ethyl glycolate, triethyl citrate, tri-n-butyl citrate, acetyltriethyl citrate, acetyl-tri-n-butyl citrate, and acetyl- tri-n-(2-ethylhexyl) citrate.

In another embodiment of the invention, the plasticizer can be one or more esters comprising: (i) at least one acid residue including residues of phthalic acid, adipic acid, trimellitic acid, succinic acid, benzoic acid, azelaic acid, terephthalic acid, isophthalic acid, butyric acid, glutaric acid, citric acid or phosphoric acid; and (ii) alcohol residues comprising one or more residues of an aliphatic, cycloaliphatic, or aromatic alcohol containing up to about 20 carbon atoms.

In another embodiment of the invention, the plasticizer can be selected from at least one of the following: esters comprising: (i) at least one acid residue selected from the group consisting of phthalic acid, adipic acid, trimellitic acid, succinic acid, benzoic acid, azelaic acid, terephthalic acid, isophthalic acid, butyric acid, glutaric acid, citric acid and phosphoric acid; and (ii) at least one alcohol residue selected from the group consisting of aliphatic, cycloaliphatic, and aromatic alcohol containing up to about 20 carbon atoms.

In another embodiment of the invention, the plasticizer can comprise alcohol residues where the alcohol residues is at least one selected from the following: stearyl alcohol, lauryl alcohol, phenol, benzyl alcohol, hydroquinone, catechol, resorcinol, ethylene glycol, neopentyl glycol, 1,4-cyclohexanedimethanol, and diethylene glycol.

In another embodiment of the invention, the plasticizer can be selected from at least one of the following: benzoates, phthalates, phosphates, arylene-bis(diaryl phosphate), and isophthalates. In another embodiment, the plasticizer comprises diethylene glycol dibenzoate, abbreviated herein as "DEGDB".

In another embodiment of the invention, the plasticizer can be selected from at least one of the following: aliphatic polyesters comprising C_{2-10} diacid residues, for example, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, and sebacic acid; and C_{2-10} diol residues.

In another embodiment, the plasticizer can comprise diol residues which can be residues of at least one of the following C_2-C_{10} diols: ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,2-butylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, neopentyl glycol, 1,5-pentanediol, 1,6 hexanediol, 1,5-pentylene glycol, triethylene glycol, and tetraethylene glycol.

In another embodiment of the invention, the plasticizer can include polyglycols, such as, for example, polyethylene glycol, polypropylene glycol, and polybutylene glycol. These can range from low molecular weight dimers and trimers to high molecular weight oligomers and polymers. In one embodiment, the molecular weight of the polyglycol can range from about 200 to about 2000.

In another embodiment of the invention, the plasticizer comprises at least one of the following: Resoflex® R296 plasticizer, Resoflex® 804 plastocizer, SHP (sorbitol hexapropionate), XPP(xylitol pentapropionate), XPA(xylitol pentaacetate), GPP(glucose pentaacetate), GPA (glucose pentapropionate) and APP (arabitol pentapropionate).

In another embodiment of the invention, the plasticizer comprises one or more of: A) from about 5 to about 95 weight % of a C_2-C_{12} carbohydrate organic ester, wherein the carbohydrate comprises from about 1 to about 3 monosaccharide units; and B) from about 5 to about 95 weight % of a C_2 –C_{12} polyol ester, wherein the polyol is derived from a C_5 or C_6 carbohydrate. In one embodiment, the polyol ester does not comprise or contain a polyol acetate or polyol acetates.

In another embodiment, the plasticizer comprises at least one carbohydrate ester and the carbohydrate portion of the carbohydrate ester is

derived from one or more compounds selected from the group consisting of glucose, galactose, mannose, xylose, arabinose, lactose, fructose, sorbose, sucrose, cellobiose, cellotriose and raffinose.

In another embodiment of the invention, the plasticizer comprises at least one carbohydrate ester and the carbohydrate portion of the carbohydrate ester comprises one or more of α-glucose pentaacetate, β-glucose pentaacetate, α -glucose pentapropionate, β-glucose pentapropionate, α-glucose pentabutyrate and β-glucose pentabutyrate.

In another embodiment, the plasticizer comprises at least one carbohydrate ester and the carbohydrate portion of the carbohydrate ester comprises an α-anomer, a β-anomer or a mixture thereof.

In another embodiment of the invention, the plasticizer can be a solid, non-crystalline resin. These resins can contain some amount of aromatic or polar functionality and can lower the melt viscosity of the cellulose esters. In one embodiment of the invention, the plasticizer can be a solid, non-crystalline compound (resin), such as, for example, rosin; hydrogenated rosin; stabilized rosin, and their monofunctional alcohol esters or polyol esters; a modified rosin including, but not limited to, maleic- and phenol-modified rosins and their esters; terpene resins; phenol-modified terpene resins; coumarin-indene resins; phenolic resins; alkylphenol-acetylene resins; and phenol-formaldehyde resins.

The amount of plasticizer in the cellulose ester additive can range from about 1 to about 50 weight percent based on the weight of the cellulose ester. Other ranges can be from about 5 to about 35 weight percent based on the weight of the cellulose ester, from about 5 to about 30, and from about 10 to about 20.

The compatibilizer can be either a non-reactive compatibilizer or a reactive compatibilizer. The compatibilizer can enhance the ability of the cellulose ester to reach a desired small particle size to improve the dispersion of the cellulose ester into an elastomer. The compatibilizers used can also improve mechanical and physical properties of the elastomeric composition

compositions by improving the interfacial interaction/bonding between the cellulose ester and the elastomer.

When non-reactive compatibilizers are utilized, the compatibilizer contains a first segment that is compatible with the cellulose ester and a second segment that is compatible with a nonpolar elastomer. The first segment contains polar functional groups, which provide compatibility with the cellulose ester, including, but not limited to, such polar functional groups as ethers, esters, amides, alcohols, amines, ketones and acetals. The first segment may consist of oligomers or polymers of the following: cellulose esters; cellulose ethers; polyoxyalkylene, such as, polyoxyethylene, polyoxypropylene, polyoxybutylene; polyglycols, such as, polyethylene glycol, polypropylene glycol, polybutylene glycol; polyesters, such as, polycaprolactone, polylactic acid, aliphatic polyesters, aliphatic-aromatic copolyesters; polyacrylates and polymethacrylates; polyacetals; polyvinylpyrrolidone; polyvinyl acetate; and polyvinyl alcohol. In one embodiment, the first segment is polyoxyethylene or polyvinyl alcohol.

The second segment is compatible with the nonpolar elastomer and contains nonpolar groups. The second segment can be either saturated or unsaturated hydrocarbon groups or contain both saturated and unsaturated hydrocarbon groups. The second segment can be an oligomer or a polymer. In one embodiment of the invention, the second segment of the non-reactive compatibilizer is selected from the group consisting of polyolefins, polydienes, polyaromatics , and copolymers. An example of a polyaromatic second segment is polystyrene. An example of a copolymer second segment is styrene/butadiene copolymer.

In one embodiment, the first and second segments of the non-reactive compatibilizers can be in a diblock, triblock, branched or comb structure. The molecular weight of the non-reactive compatibilizers can range from about 300 to about 20,000 or from about 500 to about 10,000 or from about 1,000 to about 5,000. The segment ratio of the non-reactive compatibilizers can range

from about 15 to about 85% polar first segments to about 15 to about 85% nonpolar second segments.

Examples of non-reactive compatibilizers include, but are not limited to, ethoxylated alcohols, ethoxylated alkylphenols, ethoxylated fatty acids, block polymers of propylene oxide and ethylene oxide, polyglycerol esters, polysaccharide esters, and sorbitan esters. Examples of ethoxylated alcohols are C_{11}-C_{15} secondary alcohol ethoxylates, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, and C_{12}-C_{14} natural liner alcohol ethoxylated with ethylene oxide. C_{11}-C_{15} secondary ethyoxylates can be obtained as Dow Tergitol® 15S from the Dow Chemical Company. Polyoxyethlene cetyl ether and polyoxyethylene stearyl ether can be obtained from ICI Surfactants under the Brij® series of products. C_{12}-C_{14} natural linear alcohol ethoxylated with ethylene oxide can be obtained from Hoechst Celanese under the Genapol® series of products. Examples of ethoxylated alkylphenols include octylphenoxy poly(ethyleneoxy)ethanol and nonylphenoxy poly(ethyleneoxy)ethanol. Octylphenoxy poly(ethyleneoxy)ethanol can be obtained as Igepal® CA series of products from Rhodia, and nonylphenoxy poly(ethyleneoxy)ethanol can be obtained as Igepal CO series of products from Rhodia or as Tergitol® NP from Dow Chemical Company. Ethyoxylated fatty acids include polyethyleneglycol monostearate or monolaruate which can be obtained from Henkel under the Nopalcol® series of products. Block polymers of propylene oxide and ethylene oxide can be obtained under the Pluronic® series of products from BASF. Polyglycerol esters can be obtained from Stepan under the Drewpol® series of products. Polysaccharide esters can be obtained from Henkel under the Glucopon® series of products, which are alkyl polyglucosides. Sorbitan esters can be obtained from ICI under the Tween® series of products.

In another embodiment of the invention, the non-reactive compatibilizers can be synthesized *in situ* in the cellulose ester composition or the elastomeric composition composition by reacting cellulose ester-compatible compounds with elastomer-compatible compounds. These

compounds can be, for example, telechelic oligomers, which are defined as prepolymers capable of entering into further polymerization or other reaction through their reactive end groups. In one embodiment of the invention, these *in situ* compatibilizers can have higher molecular weight from about 10,000 to about 1,000,000.

In another embodiment of the invention, the compatibilizer can be reactive. The reactive compatibilizer comprises a polymer or oligomer compatible with one component of the composition and functionality capable of reacting with another component of the composition. There are two types of reactive compatibilizers. The first reactive compatibilizer has a hydrocarbon chain that is compatible with a nonpolar elastomer and also has functionality capable of reacting with the cellulose ester. Such functional groups include, but are not limited to, carboxylic acids, anhydrides, acid chlorides, epoxides, and isocyanates. Specific examples of this type of reactive compatibilizer include, but are not limited to: long chain fatty acids, such as, stearic acid (octadecanoic acid); long chain fatty acid chlorides, such as, stearoyl chloride (octadecanoyl chloride); long chain fatty acid anhydrides, such as, stearic anhydride (octadecanoic anhydride); epoxidized oils and fatty esters; styrene maleic anhydride copolymers; maleic anhydride grafted polypropylene; copolymers of maleic anhydride with olefins and/or acrylic esters, e.g. terpolymers of ethylene, acrylic ester and maleic anhydride; and copolymers of glycidyl methacrylate with olefins and/or acrylic esters, e.g. terpolymers of ethylene, acrylic ester, and glycidyl methacrylate.

Reactive compatibilizers can be obtained as SMA® 3000 styrene maleic anhydride copolymer from Sartomer/Cray Valley, Eastman G-3015® maleic anhydride grafted polypropylene from Eastman Chemical Company, Epolene® E-43 maleic anhydride grafted polypropylene obtained from Westlake Chemical, Lotader® MAH 8200 random terpolymer of ethylene, acrylic ester, and maleic anhydride obtained from Arkema, Lotader® GMA AX 8900 random terpolymer of ethylene, acrylic ester, and glycidyl methacrylate,

and Lotarder® GMA AX 8840 random terpolymer of ethylene, acrylic ester, and glycidyl methacrylate.

The second type of reactive compatibilizer has a polar chain that is compatible with the cellulose ester and also has functionality capable of reacting with a nonpolar elastomer. Examples of these types of reactive compatibilizers include cellulose esters or polyethylene glycols with olefin or thiol functionality. Reactive polyethylene glycol compatibilizers with olefin functionality include, but are not limited to, polyethylene glycol allyl ether and polyethylene glycol acrylate. An example of a reactive polyethylene glycol compatibilizer with thiol functionality includes polyethylene glycol thiol. An example of a reactive cellulose ester compatibilizer includes mercaptoacetate cellulose ester.

The amount of compatibilizer in the cellulose ester additive can range from about 1 wt% to about 40 wt%, from about 5 wt% to about 20 wt%, or about 10 to about 20 wt% based on the weight of the cellulose ester additive.

Methylene acceptor resins can be any that is known in the art. Examples of methylene acceptor resins include, but are not limited to, melamine resins (melamine-formaldehyde resins), urea resins (urea-formaldehyde resins), polycarbonate resins, phenolic thermosetting resins, epoxy resins, unsaturated polyester resins, acrylic resins, and guanamine resins, and polyurethane resins. Phenolic thermosetting resins are those that can cure under application of heat. These phenolic thermosetting resins include a wide variation of phenol resins that include not only polycondensation products from not only phenol as a raw material, but also polycondensation products formed of a phenolic compound, such as cresol and xylenol. In one embodiment, the phenolic thermoseeting resin is prepared by reacting phenol with aldehydes, such as, formaldehyde, acetaldehyde, and furfural in the presence of an acid catalyst or alkaline catalyst. Phenolic thermosetting resins can be modified by various compounds including, but not limited to cashew oil, tall oil, linseed oil, various animal and vegetable oils, unsaturated fatty acid, rosin, an alkylbenzene

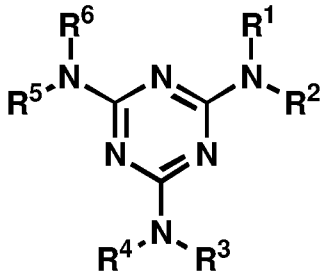
reins, aniline, and melamine. Examples of phenolic thermosetting resins include , but are not limited to, modified and unmodified phenolic resins, such as, simple or unmodified phenolic resins, cashew-modified phenolic resins, oil-modified phenolic resins, cresol modified phenolic resins, cashew-modified cresol resins, oil-modified cresol resins, novalak type xylenol resins, novalak type resorcinol resins and polyvinylphenol resins. These phenolic thermosetting resins can be modified with oils, such as, for example, rosin oil, tall oil, linseed oil, cashew oil, linoleic acid, oleic acid, linoleic acid, andvarious animal and vegetable oils.

In another embodiment of this invention, the methylene acceptor is a resole resin. Resole resins are based catalyzed phenol-formaldehyde resins having a formaldehyde to phenol ratio of greater than 1. In yet another embodiment, the methylene acceptor is a novolac resin, which is a phenol-formaldehyde resin with a formaldehyde to phenol molar ratio of less than one. The polymerization is brought to completion using acid-catalysis such as oxalic acid, hydrochloric acid or sulfonate acids. The phenol units are mainly linked by methylene and/or ether groups. Of course, phenolic resins that can be used in the present invention are not limited to those exemplified above. These phenolic resins may be used either singly or in admixture thereof in any proportions.

The amount of the methylene acceptor in the elastomeric composition may vary. The amount of the methylene acceptor in the elastomeric composition of the present invention can be at least about 0.1, 0.5, 1, 2, 3, 4, or 5 parts phr and not more than about 60, 50, 40, 30, 25, 20, or 15 phr, based on the total weight of the elastomers. In one embodiment of the invention, the amount of methylene acceptor ranges from about 0.1 to about 60 phr. Other ranges are from about 1 to about 40 phr and about 2 to about 25 phr.

The methylene donor compound is capable of reacting with the methylene acceptor. Methylene donors can be any that is known to those skilled in the art. In one embodiment of the invention, the methylene donor is

a condensation product of melamine and formaldehyde, such as dimethylol melamine, trimethylol melamine, tetramethylol melamine, and hexamethylol melamine. In another embodiment of the invention, the methylene donor is a condensation produce of melamine, formaldehyde, and methanol, such as, hexakis (methoxymethyl) melamine, pentakis(methoxymethyl)methylol melamine, and hexamethylene-tetramine. Other examples of methylene donor compounds include, but are not limited to, hexamethylenetetramine, hexamethoxymethylmelamine, hexaethoxymethylmelamine, iminomethoxymethylmelamine, imino-isobutoxymethylmelamine, lauryloxymethylpyridinium chloride, ethoxymethylpyridinium chloride, trioxan hexamethoxymethylmelamine, the hydroxy groups of which may be esterified or partly esterified, and polymers of formaldehyde such as paraformaldehyde. In addition, the methylene donors may be N-substituted oxymethylmelamines, of the general formula:



Wherein R^1, R^2, R^3, R^4, R^5, R^6 are individually selected from the group consisting of hydrogen, an alkyl having from 1 to 8 carbon atoms, and a group $–CH_2OX^n$, wherein n is 1, 2, 3, 4, 5, or 6, and wherein X^n is individually selected from the group consisting of hydrogen, and an alkyl having from 1 to 8 carbon atoms.

Specific methylene donors include hexakis-(methoxymethyl)melamine; N,N',N''-trimethyl/N,N',N''-trimethylolmelamine; hexamethylolmelamine; N,N',N''-dimethylomelamine; N-methylolmelamine, N,N'-dimethylolmelamine; N,N',N''-tris(methoxymethyl)melamine; and N,N',N''-tributyl-N,N',N''-trimethylol-melamine.

The amount of methylene donor that is present in the elastomeric composition may vary. The elastomeric composition of the present invention can comprise at least about 0.01, 0.05, 0.1, 0.15, 0.25, or 0.5 parts per hundred rubber ("phr") of at least one methylene donor, based on the total weight of the elastomers. Additionally or alternatively, the elastomeric composition of the present invention can comprise not more than about 10, 9, 7, 5, 3, or 2 phr of at least one methylene, based on the total weight of the elastomers. In other embodiments of the invention, the amount of methylene donor ranges from about 0.01 to about 10 phr, about 0.1 to about 5 phr and from about 0.1 to about 3 phr. The methylene donor can be used singly or in combination of two or more.

In certain embodiments, the elastomeric composition of the present invention can comprise one or more fillers. The fillers can comprise any filler that can improve the thermophysical properties of the elastomeric composition (e.g., modulus, strength, and expansion coefficient). For example, the fillers can comprise silica, carbon black, clay, alumina, talc, mica, discontinuous fibers including cellulose fibers and glass fibers, aluminum silicate, aluminum trihydrate, barites, feldspar, nepheline, antimony oxide, calcium carbonate, kaolin, and combinations thereof. In one embodiment, the fillers comprise an inorganic and nonpolymeric material. In another embodiment, the fillers comprise silica and/or carbon black. In yet another embodiment, the fillers comprise silica.

In certain embodiments, the elastomeric composition can comprise at least about 5, 10, 15, 20, 25, 30, 35, 40, 45, or 50 phr of one or more fillers, based on the total weight of the elastomers. Additionally or alternatively, the elastomeric composition can comprise not more than about 150, 140, 130, 120, 110, 100, 90, 80, 70, or 60 phr of one or more fillers, based on the total weight of the elastomers.

In certain embodiments, the elastomeric composition is a highly-filled elastomeric composition. As used herein, a "highly-filled" elastomeric composition comprises at least about 60 phr of one or more fillers, based on

the total weight of the elastomers. In one embodiment, a highly-filled elastomeric composition comprises at least about 65, 70, 75, 80, 85, 90, or 95 phr of one or more fillers, based on the total weight of the elastomers. Additionally or alternatively, the highly-filled elastomeric composition can comprise not more than about 150, 140, 130, 120, 110, or 100 phr of one or more fillers, based on the total weight of the elastomers.

In certain embodiments, the elastomeric composition is not highly-filled and contains minor amounts of filler. In such an embodiment, the elastomeric composition can comprise at least about 5, 10, or 15 phr and/or not more than about 60, 50, or 40 phr of one or more fillers, based on the total weight of the elastomers.

The elastomeric composition of the present invention can comprise one or more additives. In certain embodiments, the elastomeric composition can comprise at least about 1, 2, 5, 10, or 15 phr of one or more additives, based on the total weight of the elastomers. Additionally or alternatively, the elastomeric composition can comprise not more than about 70, 50, 40, 30, or 20 phr of one or more additives, based on the total weight of the elastomers.

The additives can comprise, for example, processing aids, carrier elastomers, tackifiers, lubricants, oils, waxes, surfactants, stabilizers, UV absorbers/inhibitors, pigments, antioxidants, extenders, reactive coupling agents, and/or branchers. In one embodiment, the additives comprise one or more cellulose ethers, starches, and/or derivatives thereof. In such an embodiment, the cellulose ethers, starches and/or derivatives thereof can include, for example, amylose, acetoxypropyl cellulose, amylose triacetate, amylose tributyrate, amylose tricabanilate, amylose tripropionate, carboxymethyl amylose, ethyl cellulose, ethyl hydroxyethyl cellulose, hydroxyethyl cellulose, methyl cellulose, sodium carboxymethyl cellulose, and sodium cellulose xanthanate.

In one embodiment, the additives comprise a non-cellulose ester processing aid. The non-cellulose ester processing aid can comprise, for example, a processing oil, starch, starch derivatives, and/or water. In such an

embodiment, the elastomeric composition can comprise less than about 10, 5, 3, or 1 phr of the non-cellulose ester processing aid, based on the total weight of the elastomers. Additionally or alternatively, the elastomeric composition can exhibit a weight ratio of cellulose ester to non-cellulose ester processing aid of at least about 0.5:1, 1:1, 2:1, 3:1, 4:1, 5:1, 8:1, or 10:1.

In another embodiment, the elastomeric composition can comprise a starch and/or its derivatives. In such an embodiment, the elastomeric composition can comprise less than 10, 5, 3, or 1 phr of starch and its derivatives, based on the total weight of the elastomers. Additionally or alternatively, the elastomeric composition can exhibit a weight ratio of cellulose ester to starch of at least about 0.5:1, 1:1, 2:1, 3:1, 4:1, 5:1, 8:1, 10:1, 15:1, or 20:1. In other embodiments of this invention, there is an absence of starch in the elastomeric composition.

The rubber compositions of this invention can be formulated in any conventional manner. Additionally, at least one other common additive can be added to the rubber compositions of this invention, if desired or necessary, in a suitable amount. CEA can be added in any stage of mixing. Either CEA and/or methylene acceptor(s) and/or methylene donor(s) could be master-batched with at least one elastomer before staged mixing. CEA and methylene acceptor can also be master-batched before staged mixing.

The preparation of the compositions according to the present invention may be carried out by mixing the polymer components with the possibly present reinforcing filler and the other additives according to techniques known in the art. Mixing may be carried out for instance by means of an open-mill type mixer, or by means of an internal mixer of the type with tangential (Banbury) or interpenetrating (Intermix) rotors, or in continuous mixers of the Ko-Kneader (Buss) type, or of twin-screw co-rotating or counter-rotating type. Also, any of the fillers and additives may be pre-mixed into a carrier elastomer base to make a concentrated batch and then mixed with the final formulation. The mixing and addition sequences for the components can vary. Multiple batch mixing stages can be utilized with portions of the formulation added at

each stage. The mixing temperatures can vary up to 250°C under conditions of shear sufficient to allow for adequate mixing and dispersion of the formulation components.

The elastomeric compositions according to the present invention may be vulcanized according to known techniques, and in particular with sulfur-based vulcanizing systems commonly employed for diene elastomers. To this end, after the first few thermal-mechanical working (mixing) steps, a sulfur-based vulcanizing agent is incorporated in the composition together with vulcanization activators and accelerators. In this working step, the temperature is generally kept below 125°C, to prevent undesired pre-cross-linking phenomena.

The elastomeric compositions of the present invention can be incorporated into various types of end products. In certain embodiments, elastomeric composition is formed into a tire and/or a tire component. The tire component can comprise, for example, tire tread, subtread, undertread, body plies, belts, overlay cap plies, belt wedges, shoulder inserts, tire apex, tire sidewalls, bead fillers, and any other tire component that contains an elastomer. In one embodiment, the elastomeric composition is formed into tire tread, tire sidewalls, and/or bead fillers/apex.

In certain embodiments, the elastomeric composition is incorporated into non-tire applications. Non-tire applications include, for example, a blow-out preventers, hoses, weather stripping, belts, injection molded parts, footwear, pharmaceutical closures, plant lining, flooring, power cables, gaskets, seals, rubber rollers, and architectural trims. In particular, the elastomeric compositions can be utilized in various oil field applications such as, for example, blowout preventers, pump pistons, well head seals, valve seals, drilling hoses, pump stators, drill pipe protectors, down-hole packers, inflatable packers, drill motors, O-Rings, cable jackets, pressure accumulators, swab cups, and bonded seals.

As a viscosity modifier, CEA can be used to replace liquid rubbers, fatty acid (and other) processing aids, and oils, without the negative impact on

cured rubber properties. Because of the good cured stiffness and tear resistance it builds, CEA can also be used as a partial replacement for phenolic resins and fillers without deteriorating stress softening, fatigue and hysteresis.

EXAMPLES

Test Methods:

Several tests were conducted on the elastomeric compositions produced in these Examples. The test descriptions are as follows:

Cure Rheometer: Moving die Rheometer (MDR) was performed according to ASTM D 5289. ts2 is the time it takes for the torque of the rheometer to increase 2 units above the minimum value. tc90 is the time to reach 90% of the difference between minimum to maximum torque.

Mooney Scorch Viscosity: Was measured according to ASTM D 1646.

Hardness: Shore A hardness was measured according to ASTM D2240.

Mechanical Properties: Break stress, break strain, modulus at 100%, and 200% strains were measured as per ASTM D412. The speed of testing was 500 mm/min, and the gauge length was 63.5 mm (2.5 inch). The samples were conditioned in the lab for 40 hours at 50%+/—5% humidity and 720° F. The width of specimen was 1 inch, and length was 4.5 inch.

Hot Molded Groove Trouser Tear (at 100ºC): Molded groove trouser tear (Type CP modified trouser tear test piece with a constrained path for tear) was performed according to ASTM test method D624.

Rubber Processing Analysis (RPA): Monsanto MDR 2000E Moving Die Rheometer was used. 30°C Strain Sweep was performed at 1 Hz until 15% strain was reached.

Example 1:

Elastomeric compositions containing varying amounts of cellulose ester additive were compared to elastomeric compositions not containing any CEA. The elastomeric compositions were produced according to the formulations and parameters as shown in Table 1 and Table 2.

Table 1a lists the apex elastomeric compositions tested. The reference formulation was obtained from published open literature. Three different filler systems were applied in this study including silica and carbon black. A cellulose ester additive (CEA) was added in increasing phr in compounds from 0 to 15. Table 1b lists the sidewall and tread elastomeric compositions tested.

The elastomeric compositions were mixed in a 1.5 L Kobelco Banbury mixer with 4-wing tangential rotors. The elastomeric compositions were mixed in three mixing stages as outlined in Table 1, and described in Table 2. Various performance properties of the elastomeric compositions produced in Example 1 were tested. The properties are listed in Table 3. Cured rubber samples were prepared and vulcanized using the specified cure times.

Table 1a: Apex formulations in phr.

First Stage	***1***	***2***	***3***	***4***	***5***
NR (CV60)[1]	100	100	100	100	100
N330 carbon black[2]	70	70	70		
Silica Ultrazil® VN3(cup1)[3]				70	70
Si-69[4]				5.6	5.6
CEA	0	0	15	0	15
Naphthenic Oil	10	2.5	2.5	10	2.5
Phenolic resin (Akrochem® P-86[5])	7.5	7.5	7.5	7.5	7.5
Stearic Acid	2	2	2	2	2
Antidegradant-Lanxess: Vulkanox® HS/LG[6]	1.5	1.5	1.5	1.5	1.5
Total phr	191	183.50	198.50	198.6	206.1
Second Stage					
First stage stock	191	183.50	198.50	198.6	206.1
Total phr	191	183.50	198.50	198.6	206.1
Final Stage					
Second stage stock	191	183.50	198.50	198.6	206.1
TBBS[7]	1.5	1.5	1.5	1.5	1.5
Sulfur	3	3	3	3	3
Zinc Oxide	3	3	3	3	3
Hexa®[8]	1	1	1	1	1
Total phr	199.5	192	207	206.35	213.85

[1] Natural Rubber from Akronchem Natural Rubber
[2] N330 carbon black from Columbian
[3] Ultrazil® VN3 (cup1) silica from Degussa
[4] Si-69 - sulfur-containing organosilane from Arkema
[5] Akrochem P86 reinforcing resin – cashew nut oil modified phenol-formaldehyde resin from Akronchem
[6] Vulkanoz® HS/LG - antidegradant from Lanxess
[7] TBBS accelerator from Harwich
[8] Hexa® methylene donor from Momentive Specialty Chemicals

Table 1b: Sidewall (6-7) and tread (8-10) formulations in phr.

First Stage	***6***	***7***	***8***	***9***	***10***
NR (CV60)[1]	50	50	0	0	0
Buna® CB 24(BR)[2]	50	50	30	30	30
SBR-Duradene® 738[3]			70	70	70
N330 carbon black[4]	50	50			
N234 carbon black[5]			55	55	55
Santoflex®6PPD[6]	4	4			
CEA			0	7.5	15
Tudalen®4191Oil[7]	10	10			
Tudalen®4192 Oil[8]			20	16.5	12.5
phenolic resin (Akrochem®P-86)[9]	12	12	7.5	7.5	7.5
Stearic Acid	2	2	1.5	1.5	1.5
Akronchem®MPD-100[10]	1	1	1.5	1.5	1.5
Nochek®4729 wax [11]	1	1	0.5	0.5	0.5
Zinc oxide	3	3			
Total phr	183	183	186	190	193.5
Second Stage					
First stage stock	183	183	186	190	193.5
CEA with 18wt% TEGEH)	0	12			
Total phr	183	195	186	190	193.5
Final Stage					
Second stage stock	183	195	186	190	193.5
TBBS[12]	1	1	1	1	1
Accelator DPG[13]			0.4	0.4	0.4
Sulfur	1.8	1.8	1.8	1.8	1.8
Zinc Oxide	-	-	3	3	3
Hexa®[14]	1.5	1.5	1	1	1
Total phr	185.8	197.8	193.2	197.2	200.7

[1]Natural Rubber from Akronchem Natural Rubber
[2] Buna CB 24 – solution high-cis polybutadiene polymer from Lanxess
[3]SBR-Duradene® 738 – styrene butadiene rubber from Firesyn
[4] N330 carbon black from Columbian
[5] N234 carbon black from Columbian
[6] 6PPD – anti-oxidant from Flexsys
[7]Tudalen® 4101 oil – treated distillate aromatic extract from H&R Group
[8] Tudalen® 4102 oil – treated distillate aromatic extract from H&R Group
[9] Akrochem P86 reinforcing resin – cashew nut oil modified phenol-formaldehyde resin from Akronchem
[10] Akrochem MPD-100 – antioxidant from Akrochem
[11] Nocheck 4729 wax from Sovchem
[12] TBBS – accelerator from Harwick
[13] Accelator DPG – accelerator from Harwick
[14] Hexa® methylene donor from Momentive Specialty Chemicals

Table 2a: Apex Elastomeric Composition (Samples 1-5) and Tread Elastomeric Composition (Samples 8-10) mixing procedure for 1.5L Banbury mixer.

Stage 1	
Water temperature: 80°C Rotor speed: 65 rpm	
0"	Added rubber. Mixed 30 s.
30"	Added CB/silica and oil. Mixed 60 s.
90"	Continued mixing. Added all remaining ingredients (CEA, phenolic resin). Mixed 60 s.
150"	Continued mixing. Adjusted RPM to reach and maintain 160-165°C. Mixed 150 s.
300"	Dropped batch at 300 s.
Banded on two-roll milling for 2 min (60°C, 16 to 20 rpm, 2-4 mm gap). Cooled to room temperature before proceeding to next stage.	
Stage 2	
Water temperature: 80°C Rotor speed: 70 rpm	
0"	Added half 1st stage rubber, then remaining rubber. Mixed 120 s.
120"	Continued mixing. Adjusted RPM to reach and maintain 160-165°C.
300"	Dropped batch at 300 s.
Banded on two-roll milling for 2 min (60°C, 16 to 20 rpm, 2-4 mm gap). Cooled to room temperature before proceeding to next stage.	
Final Stage	
Water temperature: 50°C Rotor speed: 35 rpm	
0"	Added 3/4 2nd stage rubber, then all curatives, then remaining rubber. Mixed.
90-120"	Dropped at 105-110°C.
Banded on two-roll milling for 2 min (60°C, 16 to 20 rpm, 2-4 mm gap). Cooled to room temperature before proceeding to next stage.	

Table 2b: Sidewall Elastomeric Composition (Samples 6-7) mixing procedure for 1.5L Banbury mixer.

Stage 1	
Water temperature: 80°C	
Rotor speed: 65 rpm	
0"	Added rubber. Mixed 30 s.
30"	Added CB and oil. Mixed 60 s.
90"	Continued mixing. Added all remaining ingredients (phenolic resin). Mixed 60 s.
150"	Continued mixing. Adjusted RPM to reach and maintain 160-165°C. Mixed 150 s.
300"	Dropped batch at 300 s.
Banded on two-roll milling for 2 min (60°C, 16 to 20 rpm, 2-4 mm gap).	
Cooled to room temperature before proceeding to next stage.	
Stage 2	
Water temperature: 80°C	
Rotor speed: 70 rpm	
0"	Added half 1st stage rubber, then all CEA, then remaining rubber. Mixed 120 s.
120"	Continued mixing. Adjusted RPM to reach and maintain 160-165°C.
300"	Dropped batch at 300 s.
Banded on two-roll milling for 2 min (60°C, 16 to 20 rpm, 2-4 mm gap).	
Cooled to room temperature before proceeding to next stage.	
Final Stage	
Water temperature: 50°C	
Rotor speed: 35 rpm	
0"	Added 3/4 2nd stage rubber, then all curatives, then remaining rubber. Mixed.
90-120"	Dropped at 105-110°C.
Banded on two-roll milling for 2 min (60°C, 16 to 20 rpm, 2-4 mm gap).	
Cooled to room temperature before proceeding to next stage.	

Table 3a: Summary of test data for apex formulations from Table 1a.

Sample #:		***1***	***2***	***3***	***4***	***5***
CEA (phr):		***0***	***0***	***15***	***0***	***15***
Oil(phr):		**10**	**2.5**	**2.5**	**10**	**2.5**
MDR (160°C)	Units					
t90	min.	4.85	4.15	5.44	2.86	3.32
Mooney Scorch (125°C)						
t2	min.	1.11	1.01	1.03	6.3	6.1
ML(1+4)	MU	71.2	85	70.9	65.2	67
Shore A Hardness (RT)						
Hardness	—	82.6	82.1	81.2	75.3	78.93
Tensile (RT)						
Tensile strength	MPa	22.35	22.10	17.8	21.5	18.7
Elongation at break	%	286.30	225	214.7	377.6	320
M100	MPa	7.90	9.93	9.58	5.71	6.69
M200	MPa	16.766	20.37	17.03	12.77	13.42
Trouser Tear (RT)						
Ave. Force	N	28.43	24.71	34.71	32.99	24.95
Trouser Tear (100°C)						
Ave. Force	N	14.80	8.51	11.38	12.96	14.53
RPA Strain Sweep (30°C)						
G' @ 5%	kPa	7415	8642	10354	5837	6785
tanδ @ 5%	—	0.18	0.197	0.198	0.139	0.134

Table 3b: Summary of test data for sidewall and tread formulations from table 1b.

Sample #:		***6***	***7***	***8***	***9***	***10***
CEA (phr):		***0***	***12***	***0***	***7.5***	***15***
Oil(phr):		***10***	***10***	***20***	***16.5***	***12.5***
MDR (160℃)	Units					
t90	min.	5.23	6.86	11.96	10.23	13.77
Mooney Scorch (130℃)						
t2	min.	5.7	8.1	17.6	14.5	11.1
ML(1+4)	MU	41.9	36.8	37.1	40.3	41.5
Shore A Stiffness (RT)						
Stiffness	—	68	73	60.4	65	67.5
Tensile (RT)						
Tensile strength	MPa	17.21	15.83	12.02	12.15	11.55
Elongation at break	%	437	416	425.16	376.14	329.3
M100	MPa	3.09	3.66	1.84	2.418	3.08
M200	MPa	6.44	7.08	3.74	5.076	6.406
Trouser Tear (RT)						
Ave. Force	N	16.59	33.9	19.36	33.49	39.82
Trouser Tear (100℃)						
Ave. Force	N	6.49	28.8	10.19	12.11	15.02
RPA Strain Sweep (30℃)						
G' @ 5%	kPa	3419	4075	2776	3448	3995
tanδ @ 5%	—	0.15	0.16	0.166	0.178	0.187

The data in Tables 3a and 3b demonstrated some desirable properties which were obtained by practicing the present invention. The CEA was used in two ways to improve elastomeric formulations as an additive to the formulation or as a replacement or partial replacement for oil. With 15phr of CEA in Sample 3, the apex formulation showed an increase in G' @ 5%, room temperature and 100°C trouser tear resistance with a significant drop on 130°C Mooney viscosity when compared to Sample 2. The improved stiffness (evidenced by G' @ 5%) is especially beneficial for formulations such as for apex as it provides high steering stability given the apex's role of transmitting a driving force from the rim to the tire during driving and holding the load on the tire. The decreased viscosity from 85MU to 70.9MU suggests CEA can be used as processing aid to improve extrudability and productivity. For instance, one or more mixing stages could be eliminated.The improved tear resistance is beneficial to cut, chip and chunk resistance. Similar findings (increase in G', room temperature and 100°C tear resistance with a significant drop on Mooney scorch viscosity) was also found for sidewall formulations when 12 phr of CEA was added with the methylene acceptor containing formulations in stage two (Samples 6-7).

When part of the oil was replaced while adding CEA, viscosity of the formulations remained constant, and there was an additional increase of G' because of the oil removal. These effects (additional increase in G' and constant viscosity) were also found for apex formulations with silica as the main filler (sample 4-5) and tread formulations (8-10).

That which is claimed is:

1. An elastomeric composition comprising at least one elastomer, at least one cellulose ester additive, at least one methylene acceptor, at least one methylene donor, and optionally, at least one filler; wherein said cellulose ester additive comprises at least one cellulose ester.
2. The elastomeric composition according to Claim 1 wherein said cellulose ester additive further comprises at least one plasticizer.
3. The elastomeric composition according to Claim 1 wherein said cellulose ester additive further comprises at least one compatibilizer.
4. The elastomeric composition according to Claim 1 wherein said cellulose ester additive further comprises at least one plasticizer and at least on compatibilizer.
5. The elastomeric composition according to Claim 1 wherein said elastomer is selected from the group consisting of polyisoprene rubber, poly(styrene-co-butadiene) rubber (SBR), polybutadiene rubber (BR), poly(isoprene-co-butadiene) rubber (IBR), styrene-isoprene-butadiene rubber (SIBR), ethylene-propylene rubber (EPM), ethylene-propylene-diene rubber (EPDM), polysulfide, nitrile rubber, propylene oxide polymers, butyl rubber, halogenated butyl rubber, brominated butyl rubber, chlorinated butyl rubber, star-branched polyisobutylene rubber, star-branched brominated butyl (polyisobutylene/isoprene copolymer) rubber; poly(isobutylene-co-p-methylstyrene) and halogenated poly(isobutylene-co-p-methylstyrene.
6. The elastomeric composition according to Claim 1 wherein said elastomer is a non-polar elastomer.
7. The elastomeric composition according to Claim 1 wherein said elastomer is a non-nitrile elastomer.
8. The elastomeric composition according to Claim 1 wherein said cellulose ester additive in said elastomeric composition ranges from about 0.5 to about 40 phr.
9. The elastomeric composition according to Claim 2 wherein said plasticizer is at least one selected from the group consisting of a phosphate plasticizer,

benzoate plasticizer, adipate plasticizer, a phthalate plasticizer, a glycolic acid ester, a citric acid ester plasticizer and a hydroxyl-functional plasticizer.

10. The elastomeric composition according to Claim 1 wherein said compatibilizer is selected from the group consisting of ethylxylated alcohols, ethoxylated alkylphenols, ethylxylated fatty acids, block polymers of propylene oxide and ethylene oxide, polyglycertol esters, polysaccharide esters, and sorbitan esters.
11. The elastomeric composition according to Claim 1 wherein said methylene acceptor resin is at least one selected from the group consisting of melamine resins (melamine-formaldehyde resins), urea resins (urea-formaldehyde resins), polycarbonate resins, phenolic thermosetting resins, epoxy resins, unsaturated polyester resins, acrylic resins, guanamine resins, and polyurethane resins.
12. The elastomeric composition according to Claim 11 wherein said phenolic thermosetting resin is at least one selected from the group consisting of modified and unmodified phenolic resins, cashew-modified phenolic resins, oil-modified phenolic resins, cresol modified phenolic resins, cashew-modified cresol resins, oil-modified cresol resins, novalak type xylenol resins, novalak type resorcinol resins, and polyvinylphenol resins.
13. The elastomeric composition according to Claim 1 wherein said methylene acceptor resin is a resole resin or novolac resin.
14. The elastomeric composition according to Claim 1 wherein the amount of said methylene acceptor ranges from about 0.1 to about 50 phr, based on the total weight of said elastomers.
15. The elastomeric composition according to Claim 1 wherein the amount of said methylene acceptor ranges from about 2 to about 25 phr, based on the total weight of said elastomers.
16. The elastomeric composition according to Claim 1 wherein said methylene donor is a condensation product of melamine and formaldehyde or a condensation produce of melamine, formaldehyde, and methanol.
17. The elastomeric composition according to Claim 1 wherein said methylene donor is at least one selected from the group consisting of hexamethylenetetramine, hexamethoxymethylmelamine, hexaethoxymethylmelamine, iminomethoxymethylmelamine, imino-isobutoxymethylmelamine, lauryloxymethylpyridinium chloride,

ethoxymethylpyridinium chloride, trioxan hexamethoxymethylmelamine, and polymers of formaldehyde.

18. The elastomeric composition of Claim 1 wherein the amount of said methylene donor ranges from about 0.01 to about 10 phr, based on the total weight of said elastomers.
19. An article comprising said elastomeric composition of Claim 1.
20. The article according to Claim 19 wherein said article is selected from the group consisting of tire components, blow-out preventers, hoses, weather stripping, belts, injection molded parts, footwear, pharmaceutical closures, plant lining, flooring, power cables, gaskets, seals, rubber rollers, architectural trims, pump pistons, well head seals, valve seals, drilling hoses, pump stators, drill pipe protectors, down-hole packers, inflatable packers, drill motors, O-Rings, cable jackets, pressure accumulators, swab cups, and bonded seals.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/014223

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B60C 1/00; C08F 291/02; C08J 5/00; C08L 1/10; C08L 1/12 (2017.01)
CPC - B60C 1/00; C08F 291/02; C08J 5/00; C08L 1/10; C08L 1/12 (2017.02)

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)
See Search History document

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)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2004/0182486 A1 (BERNARD et al) 23 September 2004 (23.09.2004) entire document	1, 5-7, 11-15, 17-20 ---------- 2-4, 8-10, 16
Y	US 2013/0131221 A1 (EASTMAN CHEMICAL COMPANY) 23 May 2013 (23.05.2013) entire document	2-4, 8-10
Y	US 2015/0083297 A1 (TOYO TIRE & RUBBER CO LTD) 26 March 2015 (26.03.2015) entire document	16

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 March 2017	31 MAR 2017
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300	Authorized officer Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774