



(51) International Patent Classification:

C07F 7/02 (2006.01)

B60C 1/00 (2006.01)

C07F 7/08 (2006.01)

DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, 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).

(21) International Application Number:

PCT/US2025/010405

(22) International Filing Date:

06 January 2025 (06.01.2025)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

63/617,841

05 January 2024 (05.01.2024)

US

Published:

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

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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, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, 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, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, 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,

(54) Title: RUBBER COMPOSITIONS CONTAINING PHLOROGLUCINOL ACETATE OR BUTYRATE FOR USE IN TIRE TREADS OF HEAVY VEHICLES

(57) Abstract: A silane-based additive, rubber formulations including the additive and tires having tread portions made with the additive, together with methods of forming those products, are provided. Uncured rubber formulations in accordance with preferred embodiments of the invention comprise (1) a rubbery primary polymer or polymer blend, such as natural rubber and/or synthetic rubber; (2) reinforcing silica filler; (3) methylene donor compound; (4) a silane containing one or more moieties of the aforementioned network forming polymer, and (5) modified phloroglucinol. In particular networks which can be generated in-situ are preferred. The cured rubber formulation should comprise the silica, having the load-bearing-path reinforcing interpenetrating polymer network coupled thereto, within the rubber matrix, and not directly to the rubber chains via sulfidic linkages.



RUBBER COMPOSITIONS CONTAINING PHLOROGLUCINOL ACETATE OR BUTYRATE FOR USE IN TIRE TREADS OF HEAVY VEHICLES

FIELD OF THE INVENTION

[001] This invention relates generally to a rubber compound for use in tires of heavy vehicles such as large truck and bus. More specifically, the present invention relates to an eco-friendly, fuel-efficient rubber compound for use in the treads of truck and bus tires that can include standard methylene donors, that does not include resorcinol, but that unexpectedly provides superior rolling resistance and hardness properties for such rubber compounds.

BACKGROUND OF THE INVENTION

[002] Increasing pressure over the several past decades to improve vehicle fuel economy and decrease emissions along with a strong sense of environmental stewardship has driven the tire and rubber industries to reduce tire rolling resistance. Corporate Average Fuel Economy (CAFE) standards, the Greenhouse Gas (GHG) protocol, other legislations promulgated by the National Highway Transportation Safety Administration (NHTSA) and the Environmental Protection Agency (EPA) in the United States, regulations promulgated by Transportation Canada and the Canadian Health Ministry, and the European Union Tyre Label in Europe, have targeted an unmet need for the accomplishment of additional augmentation in the fuel efficiency of tires, while simultaneously maintaining or improving other aspects of tire performance. One manner of determining fuel efficiency is to examine parameters related to the rolling resistance of the rubber composition. These can be determined by various mechanical properties of the rubber compositions. Simply put, the lower the rolling resistance of the rubber composition, the more fuel efficient the tire will be.

[003] Generally, it is known in the art that, by adding silica or sulfur-containing organosilane coupling agent to tire tread rubber compositions, various properties, such as wet traction and rolling resistance, can be improved. Thus, it has been shown in Japanese Patent No. 50-88 that tire treads for winter season tires have an improved slipping resistance with a silane compound containing a silicon atom and a sulfur atom is added to the rubber compound. Likewise, European Patent No. EP 0 299 074 suggested the use of an alkoxysilane functionalized in rubber compositions comprising silica as a reinforcing filler. Similarly, in US Patent No. 5,227,425, the

disclosure of which is incorporated herein by reference in its entirety, tire tread compositions are disclosed in which the rubber component is a copolymer of a conjugated diene and a vinyl-containing aromatic compound which was prepared in solution and in which the carbon black filler was partially or completely replaced with silica and a silane coupling agent that was added during mixing separately from the polymer.

[004] However, the rubber compounds disclosed in the patents above cannot meet the load indices required for heavy vehicles, such as commercial medium trucks weighing more than 13,000 lbs. or heavy-duty trucks weighing more than 26,000 lbs. These rubber compounds are more suited for small tires, such as are used on passenger cars and light trucks.

[005] In French Patent No. 3054227, phloroglucinol tri-acetate is a known compound that can be used with some silane-containing compounds. However, the patent does not use hexamethoxymethylmelamine (HMMM) as a methylene donor compound as the purpose of the patent is to provide alternatives to methylene donor compounds. Instead, the patentee adds other ingredients such as furfurals to their formulation, which are not methylene donor compounds. Finally, the French patent does not make mention of silanes anywhere. Importantly, furfurals are not a substitute for HMMM or hexamethylenetetramine (HMT) as they have no resemblance to these structures and have completely different purposes.

[006] There have been attempts to address the issue of providing high load bearing tread compositions that include silica to provide fuel efficient treads for use on tires for truck or bus applications. One such attempt is provided in U.S. Patent Application Publication No. US 2020/0140661 A1, now U.S. Patent No. 11,267,955, which discloses and claims a rubber compound containing natural rubber, a reinforcing filler such as silica that is reactive with a special silane coupling agent such as hexamethoxymethylmelamine (HMMM)-functionalized silane (i.e., not HMMM itself), and resorcinol or a resorcinol-formaldehyde resin-based secondary network. Within the patent, phloroglucinol is referenced as a potential active hydrogen-containing compound. However, it is important to note that phloroglucinol itself is not a phloroglucinolic resin. Moreover, it is noted that this patent claims hexamethoxymethyl melamine-functionalized silane reactive with a reinforcing filler. This is believed to be the novelty of that patent, which does not claim using hexamethoxymethylmelamine (HMMM) separate and apart from silane.

[007] On the other hand, resorcinol-formaldehyde resins, also referred to as RF resins or resorcinolic resins, which are formed as the reaction product of resorcinol and formaldehyde, have

been widely used in various applications including rubber compounding. In rubber compound formulations, solid RF resins have long been used to enhance rubber properties such as the adhesion properties between rubber and reinforcing materials and the physical properties in articles such as tires, belts and hose products.

[008] The issue with these resins is that resorcinol resins generally have 10 to 20% unreacted or free resorcinol. The amount of free resorcinol can be a critical factor when balancing important properties, and the presence of free resorcinol can be problematic. For example, free resorcinol easily sublimates at melting temperatures and can volatilize during rubber mixing. Such volatilization is often referred to as fuming, and thereby creates added issues with the rubber mixing process. Further, the presence of the free resorcinol contributes to the hygroscopicity of the resorcinol resin, which in turn creates storage and handling problems.

[009] Furthermore, formaldehyde has been used to produce resorcinol-formaldehyde resins for many years. In view of its widespread use, toxicity, and volatility, formaldehyde presents potential health and environmental problems. In 2011, the US National Toxicology Program described formaldehyde as known to be a human carcinogen. Thus, rubber compositions that included resorcinol or resorcinol-formaldehyde resin compounds are not accepted by some tire manufacturers today.

[0010] In response to the need to not use resorcinol or resorcinolic-formaldehyde resins, WIPO Publication No. WO2021/141934 provides for the use of phloroglucinolic resins as a substitute for resorcinol or resorcinol-formaldehyde resins, but only where no silane additives were used. That is, like many of the other patents cited hereinabove, these resins have only been suitable in rubber compositions for use in light weight vehicle tires, as no silane additives were used in those patents or tires. Without silane additives, the load indices for large truck tires cannot be met.

[0011] Accordingly, the need exists for the development of a high load-bearing rubber compound with the load-carrying capacity of reinforced natural rubber, and the fuel efficiency of silica-based tread for use in heavy vehicle (e.g., medium to heavy-duty truck and bus) tire applications.

[0012] To date, there has only been one patent application that contains both a phloroglucinolic resin and silica. That patent application has not yet been published by WIPO, but is owned by the applicant of record herein, and is suitable for many uses, including rubber compounds for use in the treads of truck and bus tires. However, it has recently been found that, while phloroglucinol

resins improve upon resorcinol, with structural considerations, it can be seen that some of the reaction sites of phloroglucinol are consumed by linkers during the process of producing the phloroglucinol resin, and therefore have some deficiencies.

SUMMARY OF THE INVENTION

[0013] To establish a highly fuel-efficient tire for heavy trucks and buses, a rubber composition containing phloroglucinol that is modified so as to not consume methylene donor binding sites, while existing as a solid at room temperature, and having a melting point lower than typical rubber masterbatch processing temperatures is desired. Such rubber compound formulations consisting of natural rubber, silica, specialty silane coupling agents, methylene donor compounds such as hexamethoxymethylmelamine (HMMM) (separate from the silane coupling agents), and a specially modified phloroglucinol have been made. Surprisingly and unexpectedly, these rubber formulations showed much better durability and hardness as compared to similar rubber compounds that included phloroglucinol resin. This invention provides a much better natural rubber-silica tread compound for truck and bus, without sacrificing any reaction sites.

[0014] At least one aspect of the present invention can be found in a rubber composition comprising (a) a rubbery polymer or blend of polymers; (b) at least one organosilane coupling agent; (c) at least one reinforcing filler that is reactive with the at least one organosilane coupling agent; (d) at least one methylene donor compound; (e) at least one modified phloroglucinol selected from the group consisting of phloroglucinol monoacetate, diacetate and triacetate and butyrate; and (f) at least one a sulfur-donating compound. In various embodiments, the rubber composition includes the ingredients above, wherein the rubbery component (a) ranges from about 25 to about 95 weight percent based on the total weight of the rubber composition; the organosilane coupling agent (b) ranges from 0.05 parts to 30 parts organosilane coupling agent (b), per 100 parts of the rubbery polymer; the reinforcing filler (c) that is reactive with the organosilane coupling agent (b) ranges from 1 part to 150 parts reinforcing filler, per 100 parts of the rubbery polymer; the methylene donor compound (d) ranges from 0.1 parts to 30 parts methylene donor compounds, per 100 parts of the rubbery polymer; the modified phloroglucinol (e) ranges from 0.1 parts to 15 parts modified phloroglucinol, per 100 parts of the rubbery polymer; and the sulfur-donating compound (f) ranges from 0.1 parts to 5 parts sulfur-donating compound, per 100 parts of the rubbery compound.

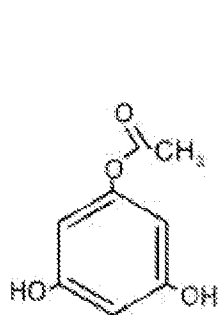
[0015] In one or more embodiments, the rubbery polymer (a) may be selected from the group consisting of natural rubber (NR), synthetic polyisoprene (IR), polybutadiene (BR), various copolymers of butadiene, the copolymers of isoprene, solution styrene-butadiene rubber (SSBR), emulsion styrene-butadiene rubber (ESBR), ethylene-propylene terpolymers (EPDM), acrylonitrile-butadiene rubber (NBR), and functionalized rubbers that are modified by at least one alkoxysilyl group, tin-containing group, amino group, hydroxyl group, carboxylic acid group, polysiloxane group, epoxy group or phthalocyanimo group. In other, more particular embodiments, the rubbery polymer includes natural rubber or a mixture of natural rubber and butadiene rubber.

[0016] In these and other embodiments, the reinforcing filler (b) may be chosen from fibers, particulates or sheet-like structures comprising metalloid oxides or metal oxides having surface hydroxyl groups. In the same or other embodiments, the reinforcing filler (b) includes precipitated silica.

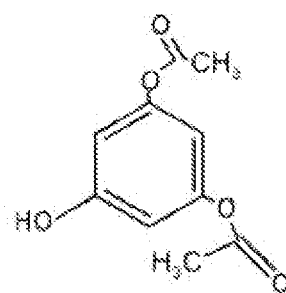
[0017] In these and other embodiments, the methylene donor compound (d) may be selected from the group consisting of hexamethoxymethylmelamine (HMMM), hexamethylenetetramine (HMT), polyisocyanates, polyisocyanurates, epoxy resins, amino resins and polyurethanes. In these and other embodiments, an amino resin may be included and selected from the group consisting of 1,1,3,3-tetra-methoxymethylurea, 1,3,3-tris-methoxymethylurea, 1,3-bis-methoxymethylurea, 1,1-bis-methoxymethylurea, 1,1,3,3-tetra-ethoxymethylurea, 1,3,3-tris-ethoxymethylurea, 1,3-bis-ethoxymethylurea, 1,1-bis-ethoxymethylurea, 1,1,3,3-tetra-propoxymethylurea, 1,3,3-tris-propoxymethylurea, 1,3-bis-propoxymethylurea, 1,1-bis-propoxymethylurea, 1,1,3,3-tetra-butoxymethylurea, 1,1,3,3-tetra-phenoxyethylurea, N-(1,3,3-tris-ethoxymethylureidomethyl)-1,3,3-tetra-ethoxymethylurea, N, N' -bis-(1,3,3-tris-ethoxymethylureidomethyl)-1,3-bis-ethoxymethylurea, N, N' -bis-(1,3,3-tris-ethoxymethylureido-methoxymethyl)-1,3-bis-ethoxymethylurea, N,N,N',N',N'',N'' -hexakis-methoxymethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N',N'',N'' -pentakis-methoxymethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N'',N'' -tetrakis-methoxymethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N',N'',N'' -hexakis-ethoxymethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N',N'',N'' -pentakis-ethoxymethyl-[1,3,5]triazine-2,4,6-triamine,

N,N,N',N'' -tetrakis-ethoxymethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N',N'',N'' -hexakis-propoxymethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N',N'',N'' -pentakis-propoxymethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N'' -tetrakis-propoxymethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N',N'',N'' -hexakis-phenoxyethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N',N'',N'' -pentakis-phenoxyethyl-[1,3,5]triazine-2,4,6-triamine and N,N,N',N'' -tetrakis-phenoxyethyl-[1,3,5]triazine-2,4,6-triamine. Most preferred of the methylene donor compounds are hexamethoxymethylmelamine (HMMM) and hexamethylenetetramine (HMT).

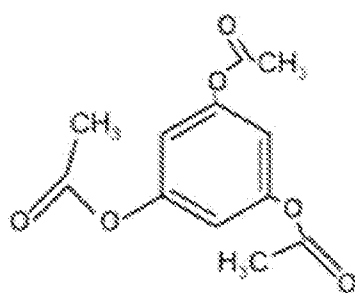
[0018] In these and other embodiments, the modified phloroglucinol (e), as defined below, may have one or more of the following structures, as set forth in Formulas (I), (II), or (III):



(I)



(II)



(III)

[0019] As noted by the structures above, it will be appreciated that the solid modified phloroglucinol used in the rubber composition may be the reaction product of a phloroglucinol and

an acetic anhydride in the presence of an acid catalyst so as to form phloroglucinol mono-acetate (as shown in Formula (I)), phloroglucinol di-acetate (as shown in Formula (II)), or phloroglucinol tri-acetate (as shown in Formula (III)) or combinations thereof.

[0020] Alternatively, it has been found that other solid modified phloroglucinols can be used in the rubber composition, which include those that are the reaction product of a phloroglucinol and a butyric anhydride in the presence of an acid catalyst so as to form phloroglucinol mono-butyrate, phloroglucinol di-butyrate, or phloroglucinol tri-butyrate, or combinations thereof.

[0021] Generally, it will be appreciated that the sulfur-donating compound (f) may be sulfur.

[0022] One or more other aspects of the present invention may be found in a process for the preparation of the rubber composition as set forth above.

[0023] Still other aspects of the present invention may be found in a cured rubber composition prepared from the rubber composition as set forth above. It will be appreciated that other aspects of the invention can be obtained by an article, such as a component of a tire, comprising this cured rubber composition.

DETAILED DESCRIPTION

[0024] Truck tires, and other heavy-duty vehicle tires include an expandable construction of multiple contractible bands of rubber and composite materials. For instance, the layer above the innerliner, consisting of thin textile fiber cords bonded into the rubber is called the carcass or casing. Carcass and casing are interchangeable terms. Many tire carcasses are one or two body plies. The tire carcass can incorporate fabric of steel, polyester, nylon or rayon cords within the carcass rubber compound. A belt system can be disposed on top of (radially outside) the carcass portion in the tire construction process. A tread slab or cap portion can be disposed on top of (radially outside) the belt system and/or carcass. The tread portion contacts the road and is formulated to enhance the performance properties and durability of the tire. Key properties include handling, traction, rolling resistance and wear resistance.

[0025] In the specification and claims herein, the following terms and expressions are to be understood as indicated.

[0026] Other than in the working examples or where otherwise indicated, all numbers expressing amounts of materials, reaction conditions, time durations, quantified properties of materials, and so forth, stated in the specification and claims are to be understood as being modified

in all instances by the term "about". Moreover, where a number in a table is provided in a claim, it will be appreciated that that number will mean "or less" where most or many of the other numbers within the same table for the same property, amount, etc. are lower than the number provided. Conversely, where a number in a table is provided in a claim, it will be appreciated that the number will mean "or more" where most or many of the other numbers within the same table for the same property, amount, etc. are higher than the number provided.

[0027] All methods described herein may be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context or unless claimed in a specific order. The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed.

[0028] No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

[0029] The term "for instance" is to have the same meaning as "for example."

[0030] It will be understood that any numerical range recited herein includes all sub-ranges within that range and any combination of the various endpoints of such ranges or sub-ranges.

[0031] As used herein, integer values of stoichiometric subscripts refer to molecular species and non-integer values of stoichiometric subscripts refer to a mixture of molecular species on a molecular weight average basis, a number average basis or a mole fraction basis.

[0032] In the description that follows, all weight percentages are based upon total weight percent of the organic material(s) unless stated otherwise and all ranges given herein comprise all subranges therebetween and any combination of ranges and/or subranges therebetween.

[0033] A "rubbery polymer", as used herein, is an organic polymer containing at least two carbon-carbon double bonds and a backbone comprising a chain or chains of carbon atoms, or mixtures thereof. In one embodiment of the invention, rubbery polymer can be at least one member selected from the group consisting of diene-based elastomers and rubbers. Rubbery polymer can be any of those that are well known in the art and are described in numerous texts, of which two examples, which are incorporated by reference herein, include natural rubber and butadiene rubber.

[0034] The term rubbery polymer does not exclude that parts of the polymer could be temporarily or permanently in a partial or complete crystalline state. The terms used in this description are, to the extent possible, the same as presented in the Vanderbilt Rubber Handbook;

R.F. Ohm, ed.; R.T. Vanderbilt Company, Inc., Norwalk, CT; 1990 and Manual For The Rubber Industry; T. Kempermann, S. Koch, J. Sumner, eds.; Bayer AG, Leverkusen, Germany; 1993.

[0035] The term primary network refers to a rubbery polymer network that is cross-linked via vulcanization by a cross-linker in the cure package.

[0036] The term interpenetrating network refers to the polymerization of rubber compound ingredients within the compound without covalent interaction with the primary network.

[0037] The term “modified phloroglucinol” is specifically defined herein as meaning a phloroglucinol that has had one or more of its -OH groups modified from -OH to form some other group such as an acetate or a butyrate. Thus, a modified phloroglucinol does not include phloroglucinolic resins, as those resins are known to bind to methylene donor binding sites and not the -OH groups.

[0038] Some representative non-limiting examples of suitable rubbery polymer, the rubber component of the composition, include those selected from the group consisting of natural rubber (NR), synthetic polyisoprene (IR), polybutadiene (BR), various copolymers of butadiene, the various copolymers of isoprene, solution styrene-butadiene rubber (SSBR), emulsion styrene-butadiene rubber (ESBR), ethylene-propylene terpolymers (EPDM), acrylonitrile-butadiene rubber (NBR) and combinations thereof. It is understood that natural rubber (NR) includes rubber from various natural plant sources, including but not limited to, rubber trees, dandelions, guayule, and so forth.

[0039] Suitable monomers for preparing the rubbery polymers herein can be selected from the group consisting of conjugated dienes such as the non-limiting examples of isoprene and 1,3-butadiene; and suitable vinyl aromatic compounds, such as the non-limiting examples of styrene and alpha methyl styrene; and combinations thereof. Rubbery polymers can be a sulfur curable rubber. The diene based elastomers, or rubbers, can be selected, to be at least one of cis-1,4-polyisoprene rubber, including natural rubber and synthetic polyisoprene rubber, and more specifically natural rubber, emulsion polymerization-prepared styrene/butadiene copolymer rubber, organic solution polymerization-prepared styrene/butadiene rubber, 3,4-polyisoprene rubber, isoprene/butadiene rubber, styrene/isoprene/butadiene terpolymer rubber, cis- 1,4-polybutadiene, medium vinyl polybutadiene rubber (35-50 percent vinyl), high vinyl polybutadiene rubber (50-75 percent vinyl), styrene/isoprene copolymers, emulsion polymerization-prepared styrene/butadiene/acrylonitrile terpolymer rubber and

butadiene/acrylonitrile copolymer rubber. Emulsion polymerization-derived styrene/butadiene rubbers (ESBR) are also contemplated as diene-based rubbers for use herein including those having a relatively conventional styrene content of 20 to 28 percent bound styrene or, for some applications, ESBR's having a medium to relatively high bound styrene content, namely, a bound styrene content of 28 to 45 percent. Emulsion polymerization-prepared styrene/butadiene/acrylonitrile terpolymer rubbers containing 2 to 40 weight percent bound acrylonitrile in the terpolymer are also contemplated as diene-based rubbers for use herein.

[0040] The rubbery polymers can also be functionalized rubbers. Functionalized rubbers are rubbers modified by at least one functional group containing an atom other than carbon or hydrogen. The functional groups are typically alkoxysilyl groups, tin-containing groups, amino groups, hydroxyl groups, carboxylic acid groups, polysiloxane groups, epoxy groups, and the like, or combinations of these functional groups. The functional groups can be introduced into the rubbery polymer during the preparation of the synthetic rubber by co-polymerizing the monomers used to make the rubber with a monomer, initiator, or termination unit containing the functional group.

[0041] Alternatively, the rubber polymers can be modified with the functional group by grafting the functional group onto the already formed rubbery polymer.

[0042] The functionalized rubbery polymer can be used in combination with other non-functionalized rubbery polymers. The mixture can contain at least about 5 to about 95 parts per hundred parts rubber of at least one styrene-butadiene rubber, which is functionalized with at least one group selected from phthalocyanino, tin-containing groups, hydroxyl, epoxy, carboxylate, amino, alkoxysilyl and sulfido groups, where the styrene content is 0 to about 12 weight percent, and from about 5 to about 95 parts per hundred rubber of at least one further rubbery polymer. The functionalized rubbery polymers (rubber) generally have a glass transition temperature (T_g) according to DSC of -120 to -10 °C in the unvulcanized state.

[0043] In another embodiment of the invention, rubbery polymer can be a diene polymer functionalized or modified by an alkoxysilane derivative. Silane-functionalized organic solution polymerization-prepared styrene-butadiene rubber and silane-functionalized organic solution polymerization-prepared 1,4-polybutadiene rubbers may be used. These rubber compositions are known; see, for example, U.S. Patent No. 5,821,290 the entire contents of which are incorporated by reference herein.

[0044] In yet another embodiment of the invention, rubbery polymer is a diene polymer functionalized or modified by a tin derivative. Tin-coupled copolymers of styrene and butadiene may be prepared, for example, by introducing a tin coupling agent during the styrene and 1,3-butadiene monomer copolymerization reaction in an organic solvent solution, usually at or near the end of the polymerization reaction. Such tin-coupled styrene-butadiene rubbers are well known to those skilled in the art; see, for example, U.S. Patent No. 5,268,439, the entire contents of which are incorporated by reference herein. In practice, at least about 50 percent, and preferably from about 60 to about 85 percent, of the tin is bonded to the butadiene units of the styrene-butadiene rubbers to create a tin-dienyl bond.

[0045] Properties of natural rubber (NR) are particularly useful in the manufacture of heavy vehicle tires, bus tires and truck tires. One important reason for this is due to the combination of natural rubber's high content of cis-1, 4-poly isoprene, its large molecular weight, and its ability to undergo strain-induced crystallization. In one embodiment of the invention, rubbery polymer comprises natural rubber, or mixtures of natural rubber and synthetic rubbers. Preferably, when the rubbery polymer is a mixture of rubbers, the rubber recipe should include at least about 10 percent by weight of natural rubber, preferably about 30 percent by weight of natural rubber, more preferably at least about 50 percent by weight of natural rubber, and still even more preferably at least about 70 percent by weight of natural rubber.

[0046] Uncured rubber compositions preferably include a reinforcing filler. Reinforcing fillers should be materials whose moduli are higher than the rubbery polymer(s) of the rubber composition and should be capable of absorbing stress when the cured rubber composition is strained. Reinforcing fillers can be materials that are reactive with the organosilane coupling agents and can include fibers, particulates and sheet-like structures. They can be composed of inorganic minerals, silicates, silica, clays, ceramics and diatomaceous earth. The reinforcing fillers that are reactive with organosilane coupling agents can be a discrete particle or group of particles in the form of aggregates or agglomerates. The organosilane coupling agent can be reactive with the surface of the filler. Particulate precipitated silica can be useful as reinforcing filler that is reactive with the organosilanes coupling agent, particularly when the silica has reactive surface silanols. The silicas may be provided in a hydrated form or be converted to a hydrated form by reaction with water. The reinforcing filler can be used in the amount of from 1 to 150 parts reinforcing filler, per 100 parts of the rubbery polymer, more specifically from 25 to 90 parts

reinforcing filler, per 100 parts of the rubbery polymer, and more specifically from 40 to 80 parts reinforcing filler, per 100 parts of the rubbery polymer.

[0047] Representative non-limiting examples of reinforcing fillers that are reactive with organosilane coupling agents include at least one metalloid oxide or metal oxide such as pyrogenic silica, precipitated silica, titanium dioxide, aluminosilicate, alumina and siliceous materials including clays and talc and combinations thereof.

[0048] In one or more embodiments herein, the reinforcing filler may be a silica used alone or in combination with one or more other fillers, e.g., organic and/or inorganic fillers that do not react with organosilane coupling agents. A representative, non-limiting example is the combination of silica and carbon black, such as for reinforcing fillers for various rubber products, including the non-limiting example of treads for tires. Alumina can be used either alone or in combination with silica. The term "alumina" herein refers to aluminum oxide, or Al_2O_3 . Use of alumina in rubber compositions is known; see, for example, U.S. Patent No. 5,116,886 and EP 631 982, the entire contents of both of which are incorporated by reference herein.

[0049] Reinforcing fillers that are reactive with the organosilane coupling agent may be used as a carrier for the organosilane coupling agent. Other fillers that can be used as carriers are non-reactive with organosilane coupling agents. The nonreactive nature of the fillers is demonstrated by the ability of organosilane coupling agents to be extracted at greater than 50 percent of the loaded silane using an organic solvent. The extraction procedure is described in U. S. Patent No. 6,005,027, the entire contents of which are incorporated by reference herein. Representative of non-reactive carriers include, but are not limited to, porous organic polymers and carbon black. The amount of organosilane coupling agent that can be loaded on the carrier is preferably between 0.1 and 70 percent and more preferably between 10 and 50 percent, based on the total weight of the carrier and organosilane coupling agent.

[0050] In one non-limiting embodiment of the invention, the other fillers that may be mixed with reinforcing filler that is reactive with the organosilane coupling agent may be essentially inert to the organosilane coupling agent with which they are admixed as is the case with carbon black or organic polymers. In another embodiment, at least two reinforcing fillers that are reactive with organosilane coupling agent can be mixed together and can be reactive therewith. Reinforcing fillers that possess metalloid hydroxyl surface functionality, such as silicas and other siliceous particulates which possess surface silanol functionality, can be used in combination with

reinforcing fillers containing metal hydroxyl surface functionality, such as alumina and other siliceous fillers.

[0051] In one embodiment of the invention, precipitated silica is utilized as reinforcing filler that is reactive with organosilane coupling agent. In a preferred embodiment of the invention, the silica fillers can be characterized by having a Brunauer, Emmett and Teller (BET) surface area, as measured using nitrogen gas, in the range of from about 40 to about 600 m²/g, preferably in the range of from about 50 to about 300 m²/g and more preferably in the range of from about 100 to about 220 m²/g. The BET method of measuring surface area, described in the Journal of the American Chemical Society, Volume 60, page 304 (1930), is the method used herein. In yet another preferred embodiment, the silica is typically characterized by having a dibutylphthalate (DBP) absorption value in a range of from about 100 to about 350, preferably from about 150 to about 300 and more preferably from about 200 to about 250. In other embodiments, the reinforcing filler that is reactive with the organosilane coupling agent may be alumina and aluminosilicate fillers, and possess a CTAB surface area in the range of from about 80 to about 220 m²/g. CTAB surface area is the external surface area as determined by cetyl trimethylammonium bromide with a pH of about 9; the method for its measurement is described in ASTM D 3849.

[0052] Mercury porosity surface area is the specific surface area determined by mercury porosimetry. In this technique, mercury is penetrated into the pores of the sample after a thermal treatment to remove volatiles. In a more specific embodiment, set-up conditions use a 100 milligram sample, remove volatiles over 2 hours at 105 °C and ambient atmospheric pressure and employ a measuring range of from ambient to 2000 bars pressure. Such evaluations can be performed according to the method described in Winslow, et al. in ASTM bulletin, p.39 (1959) or according to DIN 66133; for such an evaluation, a CARLO-ERBA Porosimeter 2000 can be used. Useful reinforcing fillers that are reactive with the silane include silica, which has an average mercury porosity specific surface area in a range of from about 100 to about 300 m²/g, preferably from about 150 to about 275 m²/g and more preferably from about 200 to about 250 m²/g.

[0053] Suitable pore size distribution for reinforcing fillers that are reactive with organosilane coupling agents, including the non-limiting examples of silica, alumina and aluminosilicate, according to such mercury porosity evaluation, is considered herein to be five percent or less of its pores having a diameter of less than 10 nm; from about 60 to about 90 percent of its pores having a diameter of from 10 to 100 nm; from about 10 to about 30 percent of its pores having a diameter

of from 100 to 1,000 nm; and, from about 5 to about 20 percent of its pores having a diameter of greater than 1,000 nm. These reinforcing fillers can normally be expected to have an average ultimate particle size in the range of from about 0.005 to about 0.075 μm , preferably of from about 0.01 to about 0.05 μm as determined by electron microscopy, although the particles can be smaller or larger in average size. Various commercially available silicas can be used herein such as those available from PPG Industries under the HI-SIL trademark, in particular, HI-SIL 210, and 243; silicas available from Solvay, e.g., ZEOSIL 1165MP; silicas available from Evonik, e.g., VN2 and VN3, etc., and silicas available from Huber, e.g., HUBERSIL 8745.

[0054] In one embodiment of the invention, the filler can comprise a reinforcing filler that is reactive with the organosilane coupling agent in the amount of from about 15 to about 95 weight percent precipitated silica, alumina and/or aluminosilicate, preferably silica and, correspondingly, from about 5 to about 85 weight percent carbon black having a CTAB value in a range of from about 80 to about 150, more preferably, the filler can comprise from about 60 to about 95 weight percent of said silica, alumina and/or aluminosilicate, preferably silica and, correspondingly, from about 40 to about 50 weight percent of carbon black. The precipitated silica, alumina and/or aluminosilicate filler and carbon black can be pre-blended or blended together during the manufacture of the vulcanized rubber. When used, carbon black can be added in amounts ranging from 0.5 parts to 10 parts carbon black, per 100 parts of the rubbery polymer.

[0055] Tire tread portions are conventionally formulated with carbon black filler. Carbon black provides tread portions with exceptional wear resistance, which leads to high mileage, long lasting tires. When silica is used as filler, the dispersion of the silica throughout the rubber matrix can be reversed to high-friction silica-silica and rubber-silica interactions. This friction can interfere with tire properties, such as rolling resistance and wear. Adding conventional silanes to tire formulations can reduce rolling resistance by limiting internal friction of silica-silica interactions and immobilizing polymer chains on the silica surface. However, not wishing to be bound by theory, it is believed that silane bonding to the rubber chains via sulfur can increase the trans content of natural rubber, as discussed in J.I. Cuneen, Rubber Chemistry and Technology, vol. 33, page 445, 1960; and J.I. Cuneen and F.W. Shipley, Journal of Polymer Science, vol. 36, page 77, 1959. This likely adversely affects performance properties such as wear resistance. Furthermore, severely restricting chain mobility could affect the ability of natural rubber to undergo strain-induced crystallization and compromise wear resistance and tear resistance.

[0056] Conventional silanes react directly to polymer chains, and worsen critical properties of the primary rubber network. Standard amino resin-resorcinol systems can reinforce the primary polymeric network with an interpenetrating network, but can be irreversibly strained and with degradation of key properties. Without being bound by theory, it is believed that organosilanes react to build an interpenetrating network that reinforces the transfer of load from one filler to another, and decreases the friction between filler aggregates. The concentration of thermosetting interpenetrating network at the filler interface attracts the thermoset where strain is least.

[0057] Rolling resistance can be lowered by hydrophobating the silica. Increasing the effective filler volume promotes wear resistance and tear resistance. Additionally, the load-bearing path reinforcing interpenetrating network can increase reinforcement and stiffness of the resulting tread under static and dynamic deformations.

[0058] This load-bearing-path reinforcing interpenetrating network polymerization is believed to grow from the reinforcing filler surface, especially silica surface, which has reacted with the organosilane coupling agents. These organosilane coupling agents can function as initiators or co-initiators during the rubber mixing and/or curing process. The resulting load-bearing path reinforcing interpenetrating network may create additional points of physical and chemical chain entanglements for the rubber phase within the immediate surrounding of fillers. These entanglements, along with the resulting interpenetrating polymeric network and the silica, are believed to create a hierarchical structure whose modulus gradient is useful for load transfer from the rubbery polymer chains to the silica during static and dynamic deformation, thereby enhancing tear and wear resistance and reducing abrasion. The interpenetrating polymer network polymerization from the filler surface can lead to the creation of a network structure on the filler surface and increases the effective filler volume. This network structure and effective filler volume result in additional reinforcement, which is also helpful for improved wear resistance.

[0059] Without being bound by theory, it is believed that such polymeric networks are formed from the reinforcing interpenetrating polymer network, methylene donor compounds and modified phloroglucinol. As a skilled person understands, a load-bearing path interpenetrating network can also be referred to as a secondary network. Without being bound by theory, a secondary network refers to two discrete polymer networks that are not distinguishable on a macroscale. A load-bearing-path reinforcing interpenetrating network of the present invention is formed from the polymer, the methylene donor compound and a modified phloroglucinol that includes, but are not

necessarily limited to, phloroglucinol mono-acetate, phloroglucinol di-acetate, or phloroglucinol tri-acetate, phloroglucinol mono-butyrate, phloroglucinol di-butyrate, or phloroglucinol tri-butyrate, and combinations thereof.

[0060] In one embodiment of the invention, methylene donor compounds are amino resins selected from the group consisting of hexamethoxymethylmelamine (HMMM) and hexamethylenetetramine (HMT). Other amino resins can be resins formed from the reaction of -NH containing compounds, formaldehyde and alcohol. More preferably, the amino resins are derived from 2,4,6-triamino-1,3,5-triazine, benzoguanamine, urea, glycoluril and poly(meth)acrylamide.

[0061] Methylene donor compounds can be used in the amount of 0.1 to 30 parts methylene donor compounds, per 100 parts of rubbery polymer, more specifically from 0.2 to 15 parts methylene donor compounds, per 100 parts of rubbery polymer, and even more specifically from 0.3 to 10 parts methylene donor compounds, per 100 parts of rubbery polymer.

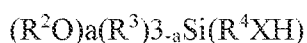
[0062] Representative and non-limiting examples of the methylene donor compounds, are hexamethoxymethylmelamine (HMMM), hexamethylenetetramine (HMT), 1,1,3,3-tetramethoxymethylurea, 1,3,3-tris-methoxymethylurea, 1,3-bis-methoxymethylurea, 1,1-bis-methoxymethylurea, 1,1,3,3-tetra-ethoxymethylurea, 1,3,3-tris-ethoxymethylurea, 1,3-bis-ethoxymethylurea, 1,1-bis-ethoxymethylurea, 1,1,3,3-tetra-propoxymethylurea, 1,3,3-tris-propoxymethylurea, 1,3-bis-propoxymethylurea, 1,1-bis-propoxymethylurea, 1,1,3,3-tetra-butoxymethylurea, 1,1,3,3-tetra-phenoxyethylurea, N-(1,3,3-tris-ethoxymethylureidomethyl)-1,1,3,3-tetra-ethoxymethylurea, N,N'-bis-(1,1,3-tris-ethoxymethylureidomethyl)-1,3-bis-ethoxymethylurea, N,N'-bis-(1,1,3-tris-ethoxymethylureido-methoxymethyl)-1,3-bis-ethoxymethylurea, N,N,N',N',N'',N''-hexakis-methoxymethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N',N'',N''-pentakis-methoxymethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N''-tetrakis-methoxymethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N',N'',N''-hexakis-ethoxymethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N',N'',N''-pentakis-ethoxymethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N''-tetrakis-ethoxymethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N',N'',N''-hexakis-propoxymethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N',N'',N''-pentakis-propoxymethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N''-tetrakis-propoxymethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N',N'',N''-hexakis-phenoxyethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N',N''-pentakis-phenoxyethyl-[1,3,5]triazine-2,4,6-triamine, N,N,N',N''-tetrakis-phenoxyethyl-[1,

3, 5]triazine-2, 4, 6-triamine, 1,3,4,6-tetrakis- methoxymethyl-tetrahydro-imidazo[4,5-d]imidazole-2,5-dione, 1,3,4,6-tetrakis-ethoxymethyl- tetrahydro-imidazo[4,5-J]imidazole-2,5-dione, 1,3,4,6-tetrakis-propoxymethyl-tetrahydro- imidazo[4,5-d]imidazole-2,5-dione, 1,3,4,6-tetrakis-phenoxyethyl-tetrahydro-imidazo[4,5- d i]imidazole-2, 5-dione, 1,3,4-tris-ethoxymethyl-tetrahydro-imidazo [4,5-d] imidazole-2, 5 -dione, 1,4-bis-ethoxymethyl-tetrahydro-imidazo[4,5-d]imidazole-2,5-dione, 1,3,4,-tris-methoxymethyl- tetrahydro-imidazo[4,5-d]imidazole-2,5-dione and 1,3,4,-tris-phenoxyethyl-tetrahydro- imidazo [4,5-d]imidazole-2,5 -dione.

[0063] Methylene donor compounds can be obtained commercially. For example, amino resins such as hexamethoxymethylmelamine (HMMM) and hexamethylenetetramine (HMT) can be commercially purchased from PERFERE, formally INEOS Melamine GmbH, under the tradenames, RESIMENE® 747 ULF, RESIMENE®755, RESIMENE®757, RESIMENE® 764, RESIMENE® CE 8824 ULF and MAPRENAL® UF 134/60B. Surprisingly, it has been found that the hardness of the rubber composition containing both HMMM and modified phloroglucinol has been found to significantly increase.

[0064] HMMM will generally attach kinetically to the 2,4, and/or 6 positions of the benzene ring of the phloroglucinol mono- di, or tri-acetate or butyrate to form a methylene bridge. However, because there may be some steric hinderance related to the acetate or butyrate group and particularly the CH₃ group thereon, it is possible that some of the HMMM will attach to various acetate or butyrate groups due to steric hindrance. Where this happens, a dimer may form. However, based upon our test results, there are very few dimers created for acetate, but not enough testing has been completed to determine that what dimers are created for butyrate.

[0065] In one instance, the organosilane coupling agents have the general Formula (IV):



(IV)

where each R² is independently hydrogen, an alkyl group having from 1 to 10 carbon atoms and optionally at least one oxygen atom, a cycloalkyl group having from 3 to 10 carbon atoms, an alkenyl group having from 2 to 10 carbon atoms, an aryl group having from 6 to 12 carbon atoms or an aralkyl group having from 7 to 12 carbon atoms, more preferably an alkyl group having from 1 to 3 carbon atoms and even more preferably ethyl; each R³ is independently an alkyl group

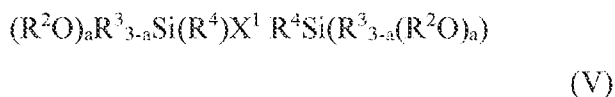
having from 1 to 3 carbon atoms or phenyl; R₄ is an alkylene group having from 1 to 10 carbon atoms and optionally at least one oxygen atom, a cycloalkylene group having from 3 to 10 carbon atoms, an alkenylene group having from 2 to 10 carbon atoms, an arylene group having from 6 to 12 carbon atoms, an aralkylene group having from 7 to 14 carbon atoms, more preferably an alkylene group having from 1 to 6 carbon atoms, and even more preferably, a propylene, X is one or more sulfur atoms, preferably between 1 and 10, and even more preferably between 1.

[0066] Representative an non-limiting examples of silane contain a functional group of Formula (IV) include 3-mercaptopropyltrimethoxysilane, 3-mercaptopropyltriethoxysilane, 3-mercaptopropyltripropoxy silane, 3-mercaptopropyl dimethoxy ethoxy silane, 3-mercaptopropyl methyl diethoxysilane, 3-mercaptopropyl dimethylethoxysilane, mercaptomethyltriethoxysilane, 4-mercaptopropyl-3,3-dimethylbutyltriethoxysilane, 3-mercaptopropylethoxy-[1,3,2]dioxasilane, 3-mercaptopropyl-(3-hydroxy-2-methylpropoxy)-5-methyl-[1,3,2]dioxasilane, 6-mercaptopropyltriethoxysilane, 3-aminopropyltriethoxysilane, N-ethyl-3-aminopropyltriethoxysilane, N-methyl-3-aminopropyltriethoxysilane, N-ethyl-3,3-dimethyl-4-aminobutyltriethoxy silane, n-phenyl-3-aminopropyltriethoxy silane, 3-ureidopropyltriethoxy silane, 3-ureidopropyltrimethoxy silane and mixtures thereof.

[0067] The silane coupling agent in formula (IV) can be used in the amounts of from 0.05 to 30 parts mercaptosilane coupling agent, per 100 parts of the rubbery polymer, more specifically, from 0.5 to 15 parts mercaptosilane coupling agent, per 100 parts rubbery polymer, and even more specifically from 1 to 10 parts mercaptosilane coupling agent, per 100 parts of the rubbery polymer.

[0068] Organosilanes of formula (Ia) can be obtained commercially. For example, mercaptosilane coupling agent can be commercially purchased from Momentive Performance Materials, Inc., under the tradenames, Si263, Usi-5301, Silquest A-189, Z-6062, KBM-803, MTMO, GENIOSIL®GF 70, and S 810.

[0069] In another instance, the organosilane coupling agents are a silane that have the general Formula (V):



where each R₂ is independently hydrogen, an alkyl group having from 1 to 10 carbon atoms and optionally at least one oxygen atom, a cycloalkyl group having from 3 to 10 carbon atoms, an

alkenyl group having from 2 to 10 carbon atoms, an aryl group having from 6 to 12 carbon atoms or an aralkyl group having from 7 to 12 carbon atoms, more preferably an alkyl group having from 1 to 3 carbon atoms and even more preferably ethyl; each R3 is independently an alkyl group having from 1 to 3 carbon atoms or phenyl; R4 is an alkylene group having from 1 to 10 carbon atoms and optionally at least one oxygen atom, a cycloalkylene group having from 3 to 10 carbon atoms, an alkenylene group having from 2 to 10 carbon atoms, an arylene group having from 6 to 12 carbon atoms, an aralkylene group having from 7 to 14 carbon atoms, more preferably an alkylene group having from 1 to 6 carbon atoms, and even more preferably, a propylene; X is one or more sulfur atoms, preferably between 2 and 10, and even more preferably between 2 and 4 on average.

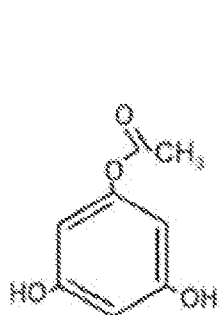
[0070] Representative and non-limiting examples of silane contain a functional group of Formula (V) include bis(tripropoxysilylpropyl)tetrasulfide; bis(triethoxysilylpropyl)tetrasulfide; bis(trimethoxysilylethyl)tetrasulfide; bis(trimethoxymethyl)tetrasulfide; bis(tripropoxysilylpropyl)disulfane; bis(triethoxysilylethyl)tetrasulfide; bis(triethoxysilylmethyl)tetrasulfide; Bis(3-triethoxysilylpropyl)disulfane; Bis[3-(triethoxysilyl)propyl]-disulfide; bis[3-(triethoxysilyl)propyl] persulfide; 3,3'-Bis-(triethoxysilylpropyl) disulfide; Bis[3-(triethoxysilyl)propyl] perdisulfide; bis(triethoxysilyl)-4,5-dithiooctane; bis(tripropoxysilylpropyl)disulfide; bis(triethoxysilylpropyl)disulfide; bis(trimethoxysilylethyl)disulfide; bis(triethoxysilylethyl)disulfide; and bis(triethoxysilylmethyl)disulfide.

[0071] The silane coupling agent in formula (V) can be used in the amounts of from 0.05 to 30 parts organosilane coupling agent, per 100 parts of the rubbery polymer, more specifically, from 0.5 to 15 parts organosilane coupling agent, per 100 parts rubbery polymer, and even more specifically from 1 to 10 parts organosilane coupling agent, per 100 parts of the rubbery polymer.

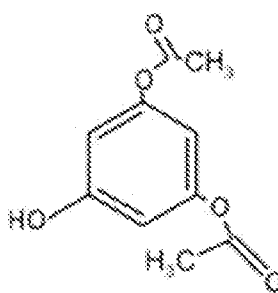
[0072] Organosilanes of formula (V) with X1 representing four sulfurs on average can be obtained commercially. For example, Si69 coupling agent can be commercially purchased from Evonik. Crosile 69 TESPT can be purchased from Guangzhou Ecopower. Z6940 can be purchased from Owen Corning Corporation. A-1289 can be purchased from Momentive Performance Materials, Inc. KBE-846 can be purchased from Shin-Etsu Co. Also, organosilanes of the formula (V) can be purchased under tradenames Si 75, HP 1589, JH-S75, TESPd for X1

[0073] Generally, the di-substituted methylene bridge is linked to at least two C1 to C10 alkyl groups extending from the methylene bridge. In another embodiment, the methylene bridge includes at least two C1 to C5 alkyl groups extending therefrom. In yet another embodiment, the methylene bridge includes at least two C1 to C4 alkyl groups extending therefrom. In still another embodiment, the methylene bridge includes at least two C1 to C3 alkyl groups extending therefrom. In yet a further embodiment, the methylene bridge includes at least two C1 to C2 alkyl groups extending therefrom.

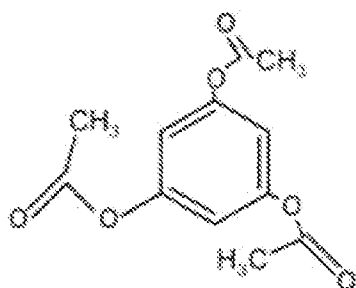
[0074] More particularly, the modified phloroglucinol of the present invention may be described as shown in Formulas (I), (II), or (III).



(I)



(II)



(III)

[0075] In other words, the modified phloroglucinol may be selected from the group consisting of mono-substituted, di-substituted, or tri-substituted phloroglucinol acetate or combinations thereof. Such modified phloroglucinol can be used in the amounts of from 0.1 to 15 parts modified phloroglucinol, per 100 parts of the rubbery polymer, more specifically, from 0.5 to 10 parts modified phloroglucinol, per 100 parts rubbery polymer, and even more specifically from 1 to 5 parts modified phloroglucinol, per 100 parts of the rubbery polymer.

[0076] Alternatively, the modified phloroglucinol may be selected from the group consisting of mono-substituted, di-substituted, or tri-substituted phloroglucinol butyrate or combinations thereof. Such modified phloroglucinol can be used in the amounts of from 0.1 to 15 parts modified phloroglucinol, per 100 parts of the rubbery polymer, more specifically, from 0.5 to 10 parts modified phloroglucinol, per 100 parts rubbery polymer, and even more specifically from 1 to 5 parts modified phloroglucinol, per 100 parts of the rubbery polymer.

[0077] A sulfur-donating compound may also be incorporated into the rubber composition. The sulfur-donating compound can be used to crosslink the rubbery polymer to form a crosslinked primary network. Without wishing to be bound by theory, the sulfur-donating compound is believed to donate sulfur atoms under curing conditions. The sulfur-donating compound generally has more than two sulfur atoms bonded together to form a chain of sulfur atoms. Polysulfides and elemental sulfur are sulfur-donating compounds, preferably sulfur, S₈.

[0078] Vulcanization can be conducted in the presence of sulfur-donating compound, often referred to as a vulcanizing agent. It reacts with the rubbery polymer containing carbon- carbon double bonds to form a crosslinked, or cured, rubber. Some non-limiting examples of suitable sulfur vulcanizing agents include, e.g., elemental sulfur (free sulfur) or sulfur-donating compound such as the non-limiting examples of amino disulfide, polymeric poly sulfide or sulfur-olefin adducts. These and other known and conventional vulcanizing agents are added in the usual amounts during a mixing step referred to as a productive mixing step in the process for preparing rubber compositions.

[0079] The sulfur-donating compounds are generally used at about 0.1 to about 5 phr, more preferably from about 1 to about 3 phr, and even more preferably from about 1.5 to about 2.5 phr.

[0080] The rubber compositions can be compounded with other commonly used additive materials such as, e.g., retarders and accelerators, processing additives such as oils, resins such as tackifying resins, plasticizers, pigments, fatty acid, zinc oxide, waxes, antioxidants and antiozonants, peptizing agents, and the like. Depending on the intended use of the rubber compositions, these and/or other rubber additives are used in conventional amounts.

[0081] Vulcanization accelerators can also be used if desired. Non-limiting examples of vulcanization accelerators include benzothiazole, alkyl thiuram disulfide, guanidine derivatives and thiocarbamates. Other examples of such accelerators include, but are not limited to, mercapto benzothiazole, tetramethyl thiuram disulfide, tetrabenzyl thiuram disulfide, benzothiazole

disulfide, diphenylguanidine, zinc dithiocarbamate, alkylphenoldisulfide, zinc butyl xanthate, N-dicyclohexyl-2-benzothiazolesulfenamide, N-cyclohexyl-2-benzothiazolesulfenamide, N-oxydiethylenebenzothiazole-2-sulfenamide, N,N-diphenylthiourea, dithiocarbamylsulfenamide, N,N-diisopropylbenzothiazole-2-sulfenamide, zinc-2-mercaptotoluimidazole, dithiobis(N-methylpiperazine), dithiobis(N-beta-hydroxy ethyl piperazine) and dithiobis(dibenzyl amine). In another embodiment, other additional sulfur donors include, e.g., thiuram and morpholine derivatives. In a more specific embodiment, representative of such donors include, but are not limited to, dimorpholine disulfide, dimorpholine tetrasulfide, tetramethyl thiuram tetrasulfide, benzothiazyl- 2,N-dithiomorpholide, thioplasts, dipentamethylenethiuram hexasulfide and disulfidecaprolactam.

[0082] Accelerators may be used to control the time and/or temperature required for vulcanization and to improve the properties of the vulcanizate. In one embodiment of the invention, a single accelerator system can be used, i.e., a primary accelerator. In another embodiment, conventionally and preferably, a primary accelerator(s) is used in total amounts ranging from about 0.5 to about 4 phr, and preferably from about 0.8 to about 2.0 phr. In a preferred embodiment, combinations of a primary and a secondary accelerator can be used with the secondary accelerator being used in smaller amounts, e.g., from about 0.05 to about 3 phr in order to activate and to improve the properties of the vulcanizate. In yet another embodiment, delayed action accelerators can also be used. In still another embodiment, vulcanization retarders can also be used. Suitable types of accelerators are those such as the non-limiting examples of amines, disulfides, guanidines, thioureas, thiazoles, thiurams, sulfenamides, dithiocarbamates, xanthates and combinations thereof. In a preferred embodiment, the primary accelerator is a sulfenamide. In another embodiment, if a second accelerator is used, the secondary accelerator can be a guanidine, dithiocarbamate or thiuram compound, such as for example tetrabenzyl thiuram disulfide used at levels from about 0.1 to about 0.3 phr, more preferably about 0.2 phr.

[0083] Optional tackifier resins can be used at levels of from about 0.5 to about 10 phr and preferably from about 1 to about 5 phr. In a preferred embodiment, the amounts of processing aids range from about 1 to about 50 phr. Suitable processing aids can include, as non-limiting examples, aromatic, naphthenic and/or paraffinic processing oils and combinations thereof. In yet another embodiment, preferred amounts of antioxidants are from about 1 to about 5 phr. Representative antioxidants include, as non-limiting examples, diphenyl-p-phenylenediamine and others, e.g.,

those disclosed in the Vanderbilt Rubber Handbook (1978), pages 344-346, which is incorporated by reference herein. In yet another embodiment, preferred amounts of antiozonants range from about 1 to about 5 phr. Preferred amounts of optional fatty acids, which can include the non-limiting example of stearic acid, range from about 0.5 to about 3 phr.

[0084] Preferred amounts of zinc oxide range from about 2 to about 5 phr. Preferred amounts of waxes, e.g., microcrystalline wax, range from about 1 to about 5 phr. Preferred amounts of peptizers range from about 0.1 to about 1 phr. Suitable peptizers include, as non-limiting examples, pentachlorothiophenol, dibenzamidodiphenyl disulfide and combinations thereof.

[0085] In one embodiment of the invention, the rubber compositions contain both a modified phloroglucinol and hexamethoxymethylmelamine, and the rubber composition preferably comprises (a) at least one rubbery polymer used to form a primary network, (b) at least one reinforcing filler that is capable of reacting with the organosilane coupling agent, (c) at least one methylene donor compound (which is the hexamethoxymethylmelamine); (d) at least one organosilane coupling agent that can be reacted with the reinforcing filler; (e) at least modified phloroglucinol selected from the group consisting of phloroglucinol monoacetate, phloroglucinol diacetate, phloroglucinol triacetate, phloroglucinol mono-butyrate, phloroglucinol di-butyrate, phloroglucinol tri-butyrate and combinations of each of the mono-, di- and tri- species; and (f) at least one sulfur-donating compound, especially sulfur (S_8) or at least one sulfur-donating compound, especially sulfur (S_8). The rubbery polymer may comprise one or more rubber components in which the rubber components add up to about 100 phr (parts per hundred rubber). In one embodiment of the invention, natural rubber should be about 50 to 100 phr of the primary polymer blend portion of the rubber composition, preferably about 75 to 100 phr. The reinforcing filler may comprise about 1 to about 150 phr of the rubber composition, preferably from about 15 to 90 phr, more preferably from about 20 to 55 phr.

[0086] Thus, in one or more embodiments, the rubber composition comprises:

- (a) a rubbery polymer or blend of polymers;
- (b) at least one organosilane coupling agent;
- (c) at least one reinforcing filler that is reactive with the organosilane coupling agent;
- (d) at least one methylene donor compound;

(e) at least one modified phloroglucinol selected from the group consisting of phloroglucinol monoacetate, phloroglucinol diacetate, phloroglucinol triacetate, and phloroglucinol butyrate; and

(f) optionally, at least one a sulfur-donating compound.

[0087] In another embodiment, the rubber composition comprises the rubbery component in an amount of from about 25 to about 95 weight percent based on the total weight of the rubber composition, the reinforcing filler that is reactive with the organosilane coupling agent in an amount of from about 2 to about 70 weight percent based on the total weight of rubber composition, the methylene donor compound in the amount of from about 0.2 to about 25 weight percent based on the total weight of the rubber composition, the modified phloroglucinol in the amount of from about 0.2 to about 25 weight percent based on the total weight of the rubber composition and the amount of the sulfur-donating compound in an amount of from about 0.2 to about 5 weight percent based on the total.

[0088] In the cured rubber composition, the primary polymeric network is cured to form a crosslinked rubber polymer or crosslinked blend of polymers by subjecting the rubber composition to an elevated temperature for a time sufficient to react the rubber polymer or blend or rubber polymers (a) with the at least one sulfur-donating compound.

[0089] In another embodiment of the invention, the process for providing the rubber compositions described herein involves the mixing the at least one reinforcing filler, the at least one methylene donor compound, the at least one organosilane coupling agent, the at least one modified phloroglucinol, and optionally, the at least one sulfur donating compound with a rubbery component, such as natural rubber, in effective amounts. In one embodiment of a process in accordance with the invention, an effective amount of organosilane coupling agent can range from about 0.2 to about 20, preferably from about 0.5 to about 15 and more preferably from about 2 to about 10, weight percent based on the total weight of rubber composition. An effective amount of rubbery component can range from about 25 to about 95, preferably from about 50 to about 90 and more preferably from about 60 to about 80, weight percent based on the total weight of the rubber composition. An effective amount of the reinforcing filler that is reactive with the organosilane coupling agent can range from about 2 to about 70, preferably from about 5 to about 55 and more preferably from about 20 to about 50, weight percent based on the total weight of rubber composition. An effective amount of the methylene donor compound can range from about 0.2 to

about 25 weight percent, preferably from about 2 to about 15 weight percent and more preferably from about 5 to about 10, weight percent based on the total weight of the rubber composition. An effective amount of the active modified phloroglucinol can range from about 0.2 to about 25 weight percent, preferably from about 2 to about 15 weight percent and more preferably from about 5 to about 10, weight percent based on the total weight of the rubber composition. An effective amount of the sulfur-donating compound can range from about 0.2 to about 5, preferably from about 0.5 to about 2.5 and more preferably from about 1 to about 2, weight percent based on the total weight of the rubber composition.

[0090] In another embodiment of the invention, the process for preparing a rubber composition can optionally comprise curing the rubber composition, before, during and/or after molding the rubber composition. A vulcanized rubber composition should contain a sufficient amount of the load-bearing-path reinforcing interpenetrating network to contribute to a higher modulus and better wear.

[0091] In one embodiment of the invention, the organosilane coupling agent is added separately to the process mixture containing rubbery polymer component. Reinforcing filler and organosilane coupling agent can be considered to couple or react in situ to form a reinforcing filler in which the organosilane coupling agent is chemically bonded to the filler.

[0092] In one embodiment of the invention, the process for preparing the rubber compositions comprise multiple steps. In the non-productive step (i), the rubbery component, reinforcing filler, and organosilane are mixed under reactive-mechanical-working conditions. As used herein, the expression "reactive-mechanical-working conditions" shall be understood to mean the conditions of elevated temperature, residence time and shear prevailing within a mechanical-working apparatus, such as an extruder, intermeshing mixer, or tangential mixer, such conditions being sufficient to bring about one or more of the following.

[0093] The reactive process of hydrolysis of organosilane coupling agent with water, which is present on the reinforcing filler, may form silanols. The reactive process of these silanols with reinforcing filler may form covalent chemical bonds with the filler. There may be a breakdown of reinforcing filler agglomerates into smaller aggregates and/or individual filler particles. Upon dispersion into the rubbery polymer, the reinforcing filler may be covalently bonded to hydrolyzed and subsequently condensed silane.

[0094] In the non-productive step (ii), the methylene donor compound and the modified phloroglucinol are added to the mixture of step (i). In the non-productive step (ii), components all the components (except sulfur donating compound in this embodiment) are mixed under reactive-mechanical-working conditions, where the conditions of elevated temperature, residence time and shear prevailing within a mechanical-working apparatus, such as an extruder, intermeshing mixer, or tangential mixer, such conditions being sufficient to bring about one or more of the following, namely, the dispersion into the mixture of the rubbery polymer, reinforcing filler covalently bonded to hydrolyzed and subsequently condensed, organosilane coupling agent of step (i) methylene donor and modified phloroglucinol; and/or the reaction of the reinforcing filler covalently bonded to hydrolyzed and subsequently condensed organosilane coupling agent with the methylene donor and the phloroglucinol resin; and/or optionally, the reaction of methylene donor with the phloroglucinol resin to form the load-bearing-path reinforcing interpenetrating network dispersed within the primary network and provide for uncured rubber composition.

[0095] If either the methylene donor or the modified phloroglucinol are not added in step (ii), then the missing ingredient can be added in a second non-productive mixing step (ii).

[0096] In the productive step (iii), the sulfur-donating compound (f) is added to the mixture of step (ii).

[0097] In any of steps (i), (ii) or (iii), other components can be added to the rubber composition. Representative and non-limiting examples of other components include activators, processing aids, accelerators, waxes, oils, anti-ozonants and anti-oxidants.

[0098] The rubber composition is typically mixed in a mixing apparatus under high shear conditions where it autogenously heats up as a result of the mixing, primarily due to shear and associated friction occurring within the rubber mixture.

[0099] In a preferred embodiment of the invention, the mixture of the desired amounts of the rubbery polymer, the reinforcing filler, the methylene donor compound and the organosilane coupling agent of step (i) is substantially homogeneously blended under reactive-mechanical-working conditions in mixing step (i) carried out on a continuous or non-continuous basis. Non-continuous mixing can be employed where a build-up of excessive heat might occur and the rubber composition may need to be cooled. Cooling of the rubber will avoid or minimize thermal decomposition of rubbery polymer component(s) or other components in the rubber composition.

Preferably, mixing step (i) is conducted at temperatures from 100 °C to 200 °C and more preferably from 140 °C to 180 °C.

[00100] In step (iii), at least one sulfur-donating compound (f) along with other vulcanization accelerators, can be mixed with the rubber composition from step (ii). Mixing should be accomplished under non-reactive-mechanical-working conditions. As used herein, the expression "non-reactive-mechanical-working" conditions shall be understood to mean the conditions of sub-ambient, ambient or slightly elevated temperature, residence time and shear prevailing within a mechanical-working apparatus, such as an extruder, intermeshing mixer, tangential mixer, or roll mill, such conditions being sufficient to bring about dispersion of the sulfur-donating compound, e.g. vulcanizing agent, and vulcanization accelerators into the rubber composition of step (ii) without resulting in any appreciable vulcanization of the rubber composition. Low temperatures and low shear are advantageously employed in step (iii).

[00101] In step (iii), residence time can vary considerably and is generally chosen to complete the dispersion of the vulcanizing agent. Residence times in most cases can range from 0.5 to 30 minutes and preferably from 5 to 20 minutes.

[00102] The temperature employed in step (iii) can range from 5 °C to 150 °C, preferably from 30 °C to 120 °C and more preferably from 50 °C to 110 °C. These temperatures are lower than those utilized for reactive-mechanical-working conditions in order to prevent or inhibit premature curing of the sulfur-curable rubber, sometimes referred to as scorching of the rubber composition, which might take place at higher temperatures.

[00103] The rubber composition may be allowed to cool, e.g., during or after step (iii) or between step (i) and step (ii) or between step (ii) and step (iii), to a temperature of 50 °C or less.

[00104] In another embodiment of the invention, when it is desired to mold and to cure the rubber composition, the rubber composition is placed in the desired mold and heated to at least about 130 °C and up to about 200 °C for a time of from 1 to 60 minutes to bring about the vulcanization of the rubber.

[00105] Rubber compositions preferred for forming tire tread portions in accordance with preferred embodiments of the invention comprise (a) a rubbery primary polymer or blend of polymers, (b) reinforcing silica filler particles, (c) an methylene donor compound, (d) a organosilane coupling agent which can react with the reinforcing filler and/or (e) an active

compound, namely, at least one modified phloroglucinol, in which components (b), (c), (d) and (e) contribute to the aforementioned load-bearing-path reinforcing interpenetrating network.

[00106] The rubber composition herein can be used for various purposes. In one embodiment of the invention, there is provided an article of which at least one component is the herein described cured rubber composition. In another embodiment herein, there is provided a tire at least one component of which, e.g., the tread, is the herein described cured rubber composition.

[00107] In yet another preferred embodiment, for example, the rubber composition can be used for the manufacture of such articles as shoe soles, hoses, seals, cable jackets, gaskets and other industrial goods. Such articles can be built, shaped, molded and cured by various known and conventional methods as is readily apparent to those skilled in the art. In particular, the compositions and methods in accordance with the invention are particularly well suited for the manufacture of tires, in particular, truck or bus tires.

EXAMPLES

[00108] In order to demonstrate the practice of the present invention, the following examples have been prepared and tested. The examples should not, however, be viewed as limiting the scope of the invention. The claims will serve to define the invention.

Modified Phloroglucinol - Examples 1 and 2.

[00109] Under the N₂ atmosphere, 50.0 g of phloroglucinol, 121.0 g of acetic anhydride for Example 1 and 121.0 g of butyric anhydride for Example 2, and 0.25 g of pyridine, were charged to a flask and heated to 100 °C. The reaction mixture was maintained at about 100°C for 1 hours. Solvent was then removed by vacuum distillation to 160 °C. When a temperature of 160 °C was reached, the vacuum was released and the liquid was discharged from the flask. After the cooling, 74.9 g phloroglucinol triacetate white crystal was obtained. The purity is confirmed by LC and NMR.

[00110] Rubber compounds containing the phloroglucinol triacetate (Example 1), the phloroglucinol butyrate (Example 2), and other control example is prepared with the usual mixing method which is well known. Rubber compositions are shown in TABLE 1. More particularly, in

a first mixing, natural rubber, silica and/or carbon black (N121), a rubber processing oil (TDAE Oil), and silane (Si69) are mixed. To that first mixing, carbon black, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) (an antioxidant), 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), a microcrystalline wax, zinc oxide, stearic acid, and where applicable, either a phloroglucinol acetone resin (for the comparison) or a phloroglucinol acetate (for Example 1 of the present invention) or a phloroglucinol butyrate (for Example 2 of the present invention), are mixed with the first mixing to provide a second mixing. To that second mixing, hexamethoxymethylmelamine (HMMM) may be added as a third mixing. And finally, sulfur, together with N-Cyclohexyl-2-benzothiazolesulfenamide (CBS) and Diphenylguanidine (DPG), is added.

[00111] For comparison, natural rubber carbon black-based rubber compositions and a rubber composition containing the comparative phloroglucinol acetone resin were then tested as against the rubber compositions of the present invention containing phloroglucinol acetate (Example 1) or phloroglucinol butyrate (Example 2) as set forth in TABLE 1.

[00112] The resultant rubber performance based upon the preparation of a vulcanized rubber as set forth below is also provided in TABLE 2. It will be appreciated that T₉₀ was measured with the Alpha Technologies MDR Rheometer (MDR2000) at 150°C, 0.5° arc and 1.6 Hz according to ASTM D-5289. The rubber compounds were cured at 150 °C, 10 tons pressure, according to parameters obtained from the MDR2000 rheometric test data. G' and tan δ, an indicator of compound hysteresis or heat build-up, was measured with a TA Instruments rheometer (ARES) at 2.0% torsional shear strain at 1Hz and 60°C and was measured shore A Hardness according to ASTM D-2240.

[00113] TABLE 1 – Composition of Examples 1-3.

Mixer volume	1570	CARBON	TESPT	TESPT (EX.1)	TESPT (EX. 2)
Material	Description	BLACK	PDL593	PG-Acetate	PG Butyrate
1st					
Natural Rubber		100.0	100.0	100.0	100.0
Silica	7000GR	0.0	50.0	50.0	50.0
Carbon Black N121		30.0	5.0	5.0	5.0
TADE Oil		1.0	1.0	1.0	1.0
Si69		0.0	4.0	4.0	4.0
MB1 Total		131.0	160.0	160.0	160.0
2nd					
1st compound		131.0	160.0	160.0	160.0
Carbon Black N121		25.0	5.0	5.0	5.0
6PPD		2.0	2.0	2.0	2.0
TMQ		0.5	0.5	0.5	0.5
Microcrystalline Wax		1.3	1.3	1.3	1.3
ZnO		3.0	3.0	3.0	3.0
Stearic Acid		2.0	2.0	2.0	2.0
Phloroglucinol Acetone Resin		0.0	3.0	0.0	0.0
Phloroglucinol Acetate		0.0	0.0	3.0	0.0
Phloroglucinol Butyrate		0.0	0.0	0.0	3.0
MB2 Total		164.8	176.8	176.8	176.8
3rd					
2nd compound		164.8	176.8	176.8	176.8
PDL593		0.0	0.0	0.0	0.0
HMMM		0.0	2.0	2.0	2.0
MB3 Total		164.8	178.8	178.8	178.8
4th					
4th compound		164.8	178.8	178.8	178.8
Sulfur		1.6	1.6	1.6	1.6
CBS		0.6	2.0	2.0	2.0
DPG		0.4	0.4	0.4	0.4
MB4 Total		167.4	182.8	182.8	182.8

[00114] TABLE 2 – Comparison of Properties of Examples 1-3

	CARBON BLACK	PDL593 / HMMM	PG ACETATE/ HMMM	PG BUTYRATE/ HMMM
Hardness	65	62	66	68
50% MOD	1.7	1.9	2.1	1.95
300% MOD	17	22	22	17.2
Elongation	494	434	405	507
tan δ 60C (2 radians)	0.17	0.06	0.06	0.085
Mooney Viscosity	23	48	33	26

[00115] In comparison between the two phloroglucinol triacetate/tributyrate samples of the present invention and those of the comparative examples, it will be appreciated that both the phloroglucinol triacetate and phloroglucinol butyrate of the present invention show unexpectedly and significantly much better hardness and Modulus at 50% compared to the carbon black and phloroglucinol resin. The phloroglucinol triacetate also shows significantly better Modulus at 300%. More surprisingly, phloroglucinol shows poor results to the conventional resorcinol formaldehyde resin. Because of this, the results for phloroglucinol triacetate and butyrate are totally unexpected.

[00116] The resultant rubber performance based upon the preparation of a vulcanized rubber as set forth below is also provided in TABLE 2. It will be appreciated that T₉₀ was measured with the Alpha Technologies MDR Rheometer (MDR2000) at 150°C, 0.5° arc and 1.6 Hz according to ASTM D-5289. The rubber compounds were cured at 150 °C, 10 tons pressure, according to parameters obtained from the MDR2000 rheometric test data. G' and tan δ , an indicator of compound hysteresis or heat build-up, was measured with a TA Instruments rheometer (ARES) at 2.0% torsional shear strain at 1Hz and 60°C and was measured shore A Hardness according to ASTM D-2240.

[00117] It can be seen that hardness is higher in the rubber composition of the present invention containing phloroglucinol acetate and HMMM, as compared to the carbon black rubber composition or rubber composition containing phloroglucinolic resin. Hardness correlates with tread wear.

CLAIMS

What is claimed is:

1. A rubber composition comprising:
 - (a) a rubbery polymer or blend of polymers;
 - (b) at least one organosilane coupling agent;
 - (c) at least one reinforcing filler that is reactive with the at least one organosilane coupling agent;
 - (d) at least one methylene donor compound;
 - (e) at least one modified phloroglucinol selected from the group consisting of phloroglucinol monoacetate, phloroglucinol diacetate, phloroglucinol triacetate and phloroglucinol butyrate and
 - (f) at least one a sulfur-donating compound;wherein a hardness of the rubber composition is increased when compared with a rubber composition having a phloroglucinolic resin.
2. The rubber composition of claim 1, wherein the rubbery component (a) ranges from about 25 to about 95 weight percent based on the total weight of the rubber composition; the organosilane coupling agent (b) ranges from 0.05 parts to 30 parts organosilane coupling agent (b), per 100 parts of the rubbery polymer; the reinforcing filler (c) that is reactive with the organosilane coupling agent (b) ranges from 1 part to 150 parts reinforcing filler, per 100 parts of the rubbery polymer; the methylene donor compound (d) ranges from 0.1 parts to 30 parts methylene donor compounds, per 100 parts of the rubbery polymer; the modified phloroglucinol (e) ranges from 0.1 parts to 10 parts modified phloroglucinol, per 100 parts of the rubbery polymer; and the sulfur-donating compound (f) ranges from 0.1 parts to 5 parts sulfur-donating compound, per 100 parts of the rubbery compound.
3. The rubber composition of claim 2, wherein the rubbery polymer (a) is selected from the group consisting of natural rubber (NR), synthetic polyisoprene (IR), polybutadiene (BR), various copolymers of butadiene, the copolymers of isoprene, solution styrene-butadiene rubber (SSBR), emulsion styrene-butadiene rubber (ESBR), ethylene-propylene terpolymers (EPDM), acrylonitrile-butadiene rubber (NBR), and functionalized rubbers that are modified by at least one

alkoxysilyl group, tin-containing group, amino group, hydroxyl group, carboxylic acid group, polysiloxane group, epoxy group or phthalocyanimo group.

4. The rubber composition of claim 2, wherein the rubbery polymer (a) comprises natural rubber or a mixture of natural rubber and butadiene rubber.

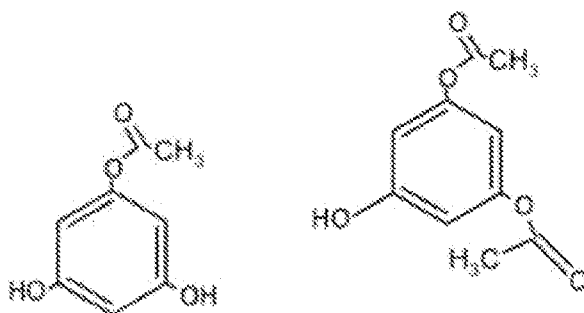
5. The rubber composition of claim 2, wherein the reinforcing filler (c) is chosen from fibers, particulates or sheet-like structures comprising metalloid oxides or metal oxides having surface hydroxyl groups.

6. The rubber composition of claim 5, wherein the reinforcing filler (c) comprises precipitated silica.

7. The rubber composition of claim 2, wherein the methylene donor compound (d) is selected from the group consisting of polyisocyanates, polyisocyanurates, epoxy resins, amino resins and polyurethanes.

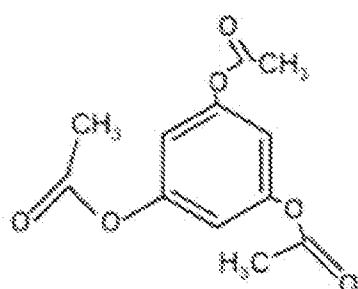
8. The rubber composition of claim 7, wherein the amino resin is selected from the group consisting of hexamethoxymethylmelamine (HMMM) and hexamethylenetetramine (HMT).

9. The rubber composition of claim 2, wherein the modified phloroglucinol (e) has the structure selected from the group consisting of Formula (I) (II) and (III):



(I)

(II)



(III)

10. The rubber composition of claim 9, wherein the modified phloroglucinol is a solid.
11. The rubber composition of claim 2, wherein the solid modified phloroglucinol is the reaction product of a phloroglucinol and acetic anhydride in the presence of a base catalyst.
12. The rubber composition of claim 2, wherein the solid modified phloroglucinol is the reaction product of a phloroglucinol and butyric anhydride in the presence of a base catalyst.
13. The rubber composition of claim 11, wherein the solid modified phloroglucinol is selected from the group consisting of phloroglucinol mono-acetate, phloroglucinol di-acetate, phloroglucinol tri-acetate and combinations thereof.
14. The rubber composition of claim 12, wherein the solid modified phloroglucinol is selected from the group consisting of phloroglucinol mono-butyrate, phloroglucinol di-butyrate, phloroglucinol tri-butyrate and combinations thereof.
15. The rubber composition of claim 2, wherein the sulfur-donating compound (f) is sulfur.

16. A process for the preparation of the rubber composition of claim 2.
17. A cured rubber composition prepared from the composition of claim 2.
18. An article comprising the cured rubber composition of claim 17.
19. The article of claim 18, wherein said article is a component of a tire.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2025/010405

A. CLASSIFICATION OF SUBJECT MATTERIPC: **C07F 7/02** (2025.01); **C07F 7/08** (2025.01); **B60C 1/00** (2025.01)CPC: **C07F 7/02**; **C07F 7/08**; **B60C 1/0016**; **B60C 11/0008**

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

See Search History Document

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.
Y	US 2005/0154151 A1 (DURAIRAJ ET AL.) 14 July 2005 (14.07.2005) entire document especially para [0042], [0019], [0018], [0046], [0049], [0066], abstract, and Table 1	1-10, 15-19
A	entire document especially para [0042], [0019], [0018], [0046], [0049], [0066], abstract, and Table 1	11-14
P,A	WO 2024/015956 A1 (SUMITOMO CHEMICAL ADVANCED TECHNOLOGIES LLC, D.B.A. SUMIKA ELECTRONIC MATERIALS) 18 January 2024 (18.01.2024) entire document	1-19
A	US 2007/0219306 A1 (DURAIRAJ ET AL.) 20 September 2007 (20.09.2007) entire document	1-19
A	US 2016/0083563 A1 (FISCHERWERKE GMBH & CO. KG) 24 March 2016 (24.03.2016) entire document	1-19
A	US 2022/0259414 A1 (PIRELLI TYRE S.P.A.) 18 August 2022 (18.08.2022) entire document	1-19



Further documents are listed in the continuation of Box C.



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“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

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Date of the actual completion of the international search

11 March 2025 (11.03.2025)

Date of mailing of the international search report

18 March 2025 (18.03.2025)

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2025/010405

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Gerd Leston, "(Polyhydroxy)benzenes" Kirk-Othmer Ency. Chem. Tech.; pp 1-38. 4 December 2000 entire document especially page 6, 19, 17, 16	1-10, 15-19
A	Gerd Leston, "(Polyhydroxy)benzenes" Kirk-Othmer Ency. Chem. Tech.; pp 1-38. 4 December 2000 entire document especially page 6, 19, 17, 16	11-14