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(54) SILICA-FILLED RUBBER COMPOSITION AND METHOD FOR MAKING THE SAME

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(57) ABSTRACT

Disclosed is a method of preparing a rubber composition comprising the steps of (a) blending in at least one preparatory mixing step at least one natural or synthetic rubbery polymer, a silica filler, a silica coupling agent, and at least one vulcanization accelerator; and (b) subsequently blending therewith in a final mixing step a sulfur curative, wherein the final mixing step is void of any vulcanization accelerator.

SILICA-FILLED RUBBER COMPOSITION AND METHOD FOR MAKING THE SAME

FIELD OF THE DISCLOSURE

[0001] This disclosure generally relates to a silica-filled rubber composition, and a method of making the same.

BACKGROUND

[0002] Reinforcing fillers, such as carbon black and silica, are commonly introduced to confer certain favorable mechanical properties to cured rubber compositions. When used alone or in combination with carbon black, silica reinforcement may provide improved traction characteristics and rolling resistance when applied in tire components.

[0003] Rubber compositions containing silica are generally prepared in at least two mixing stages—at least one preparatory mixing step in which polymers, fillers, coupling agents, plasticizers, and the like are kneaded together, and a final mixing step in which vulcanization agents such as curatives and vulcanization accelerators are added. In practice, addition of vulcanization accelerators in any preparatory mixing stage is generally disfavored to avoid premature vulcanization.

SUMMARY

[0004] Disclosed is a method of preparing a rubber composition comprising:

- **[0005]** a. blending in at least one preparatory mixing step
  - **[0006]** (i) at least one natural or synthetic rubbery polymer,
  - **[0007]** (ii) a silica filler,
  - **[0008]** (iii) a silica coupling agent, and
  - **[0009]** (iv) at least one vulcanization accelerator; and
- **[0010]** b. subsequently blending therewith in a final mixing step a sulfur curative,

wherein the final mixing step is void of any vulcanization accelerator.

[0011] Also disclosed is a rubber composition produced by a method comprising:

- **[0012]** a. blending in at least one preparatory mixing step
  - **[0013]** (i) at least one natural or synthetic rubbery polymer,
  - **[0014]** (ii) a silica filler,
  - **[0015]** (iii) a silica coupling agent, and
  - **[0016]** (iv) at least one vulcanization accelerator; and
- **[0017]** b. subsequently blending therewith in a final mixing step a sulfur curative,

wherein the final mixing step is void of any vulcanization accelerator.

[0018] Further disclosed is a tire tread comprising a rubber composition produced by a method comprising:

- **[0019]** a. blending in at least one preparatory mixing step
  - **[0020]** (i) at least one natural or synthetic rubbery polymer,
  - **[0021]** (ii) a silica filler,
  - **[0022]** (iii) a silica coupling agent, and
  - **[0023]** (iv) at least one vulcanization accelerator; and
- **[0024]** b. subsequently blending therewith in a final mixing step a sulfur curative,

wherein the final mixing step is void of any vulcanization accelerator.

[0025] Other aspects of the present disclosure will be apparent to the ordinarily skilled artisan from the description that follows. To assist in understanding the description of various embodiments that follow, certain definitions are provided immediately below. These are intended to apply throughout unless the surrounding text explicitly indicates a contrary intention:

[0026] "polymer" means the polymerization product of one or more monomers and is inclusive of homo-, co-, ter-, tetra-polymers, etc.;

[0027] "copolymer" means a polymer that includes mer units derived from two reactants, typically monomers, and is inclusive of random, block, segmented, graft, gradient, etc., copolymers; and

[0028] "phr" means parts by weight of a referenced material per 100 parts by weight rubber, and is a recognized term by those having skill in the rubber compounding art.

[0029] The terms "rubber composition" and "rubber compound" may be used interchangeably.

[0030] All references incorporated herein by reference are incorporated in their entirety unless otherwise stated.

DETAILED DESCRIPTION

[0031] Disclosed is a method of preparing a rubber composition comprising the steps of (a) blending in at least one preparatory mixing step at least one natural or synthetic rubbery polymer, a silica filler, a silica coupling agent, and at least one vulcanization accelerator; and (b) subsequently blending therewith in a final mixing step a sulfur curative, wherein the final mixing step is void of any vulcanization accelerator.

[0032] The natural or synthetic rubbery polymer can be any polymer suitable for use in a cap ply rubber composition. Examples of rubbery polymers that may be used in the compositions described herein include, but are not limited to, natural rubber, synthetic polyisoprene rubber, styrene-butadiene rubber (SBR), styrene-isoprene rubber, styrene-isoprene-butadiene rubber, butadiene-isoprene-styrene terpolymer, butadiene-isoprene rubber, polybutadiene, butyl rubber, neoprene, acrylonitrile-butadiene rubber (NBR), silicone rubber, the fluoroelastomers, ethylene acrylic rubber, ethylene-propylene rubber, ethylene-propylene terpolymer (EPDM), ethylene vinyl acetate copolymer, epichlorohydrin rubber, chlorinated polyethylene-propylene rubbers, chlorosulfonated polyethylene rubber, hydrogenated nitrile rubber, and terafluoroethylene-propylene rubber. A mixture of rubbery polymers may be used.

[0033] The rubber composition contains a silica filler. Examples of reinforcing silica fillers which can be used include wet silica (hydrated silicic acid), dry silica (anhydrous silicic acid), calcium silicate, and the like. Among these, precipitated amorphous wet-process, hydrated silicas are preferred. Silica can be employed in an amount of about 1 to about 100 phr, in an amount of about 5 to about 80 phr, or alternatively in an amount of about 30 to about 80 phr. The useful upper range is limited by the high viscosity imparted by fillers of this type. Some of the commercially available silicas which can be used include, but are not limited to, HiSil® 190, HiSil® 210, HiSil® 215, HiSil® 233, HiSil® 243, and the like, produced by PPG Industries (Pittsburgh, Pa.). A number of useful commercial grades of different silicas are also available from DeGussa Corporation (e.g., VN2, VN3), Rhone Poulenc (e.g., Zeosil® 1165MP0), and J. M. Huber Corporation.

[0034] In addition to the silica filler, carbon black may also be added to the rubber composition. The carbon black is typically added in at least one preparatory mixing step.

[0035] Carbon black, when present, may be used in an amount of about 1 to about 200 phr, in an amount of about 5 to about 100 phr, or alternatively in an amount of about 30 to about 80 phr. Suitable carbon blacks include commonly available, commercially-produced carbon blacks, but those having a surface area of at least 20 m^2/g, or preferably, at least 35 m^2/g up to 200 m^2/g or higher are preferred. Among useful carbon blacks are furnace blacks, channel blacks, and lamp blacks. A mixture of two or more carbon blacks can be used. Exemplary carbon blacks include, but are not limited to, N-110, N-220, N-339, N-330, N-352, N-550, N-660, as designated by ASTM D-1765-82a.

[0036] If the rubber composition contains a blend of silica filler and carbon black, the ratio of silica to carbon black may range from about 0.1:1 to about 10:1, or from about 1:1 to about 10:1, or from about 5:1 to about 10:1.

[0037] The surface of the carbon black and/or silica may optionally be treated or modified to improve the affinity to particular types of polymers. Such surface treatments and modifications are well known to those skilled in the art.

[0038] Additional fillers may also be utilized, including but not limited to, mineral fillers, such as clay, talc, aluminum hydrate, aluminum hydroxide and mica. The foregoing additional fillers are optional and can be utilized in varying amounts from about 0.5 phr to about 40 phr.

[0039] The total amount of filler may be from about 1 to about 200 phr, alternatively from about 5 to about 100 phr, from about 10 phr to about 30 phr, from about 30 to about 80 phr, or from about 40 to about 70 phr.

[0040] A silica coupling agent is used to couple the silica to the rubbery polymer. Numerous coupling agents are known, including but not limited to organosulfide polysulfides and organoalkoxymercaptosilanes. Any organosilane polysulfide may be used. Suitable organosilane polysulfides include, but are not limited to, 3,3'-bis(trimethoxysilylpropyl)disulfide, 3,3'-bis(triethoxysilylpropyl)disulfide, 3,3'-bis(triethoxysilylpropyl)tetrasulfide, 3,3'-bis(triethoxysilylpropyl)octasulfide, 3,3'-bis(trimethoxysilylpropyl)tetrasulfide, 2,2'-bis(triethoxysilylethyl)tetrasulfide, 3,3'-bis(trimethoxysilylpropyl) trisulfide, 3,3'-bis(triethoxysilylpropyl)trisulfide, 3,3'-bis (tributoxysilylpropyl)disulfide, 3,3'-bis (trimethoxysilylpropyl)hexasulfide, 3,3'-bis (trimethoxysilylpropyl)octasulfide, 3,3'-bis (trioctoxysilylpropyl)tetrasulfide, 3,3'-bis (trihexoxysilylpropyl)disulfide, 3,3'-bis(tri-2"-ethylhexoxysilylpropyl)trisulfide, 3,3'-bis (triisooctoxysilylpropyl)tetrasulfide, 3,3'-bis(tri-t-butoxysilylpropyl)disulfide, 2,2'-bis (methoxydiethoxysilylethyl)tetrasulfide, 2,2'-bis (tripropoxysilylethyl)pentasulfide, 3,3'-bis (tricycloneoxysilylpropyl)tetrasulfide, 3,3'-bis (tricyclopentoxysilylpropyl)trisulfide, 2,2'-bis(tri-2"-methylcyclohexoxysilylethyl)tetrasulfide, bis (trimethoxysilylmethyl)tetrasulfide, 3-methoxyethoxypropoxysilyl 3'-diethoxybutoxy-silylpropyl tetrasulfide, 2,2'-bis(dimethylmethoxysilylethyl)disulfide, 2,2'-bis(dimethylsecbutoxysilylethyl) trisulfide, 3,3'-bis (methylbutylethoxysilylpropyl)tetrasulfide, 3,3'-bis(di t-butylmethoxysilylpropyl) tetrasulfide, 2,2'-bis(phenylmethylmethoxysilylethyl)trisulfide, 3,3'-bis(diphenyl isopropoxysilylpropyl)tetrasulfide, 3,3'-bis(diphenylcyclohexoxysilylpropyl)disulfide, 3,3'-bis (dimethylethylmercaptosilylpropyl)tetrasulfide, 2,2'-bis (methyldimethoxysilylethyl)trisulfide, 2,2'-bis(methyl ethoxypropoxysilylethyl)tetrasulfide, 3,3'-bis(diethylmethoxysilylpropyl)tetrasulfide, 3,3'-bis(ethyldi-secbutoxysilylpropyl)disulfide, 3,3'-bis(propyldiethoxysilylpropyl) disulfide, 3,3'-bis(butyldimethoxysilylpropyl)trisulfide, 3,3'-bis(phenyldimethoxysilylpropyl)tetrasulfide, 3'-trimethoxysilylpropyl tetrasulfide, 4,4'-bis(trimethoxysilylbutyl)tetrasulfide, 6,6'-bis(triethoxysilylhexyl)tetrasulfide, 12,12'-bis (triisopropoxysilyldodecyl)disulfide, 18,18'-bis (trimethoxysilyloctadecyl)tetrasulfide, 18,18'-bis (tripropoxysilyloctadecenyl)tetrasulfide, 4,4'-bis (trimethoxysilyl-buten-2-yl)tetrasulfide, 4,4'-bis (trimethoxysilylcyclohexylene)tetrasulfide, 5,5'-bis (dimethoxymethylsilylpentyl)trisulfide, 3,3'-bis (trimethoxysilyl -2-methylpropyl)tetrasulfide and 3,3'-bis (dimethoxyphenylsilyl-2-methylpropyl)disulfide.

[0041] Suitable organoalkoxymercaptosilanes include, but are not limited to, triethoxy mercaptopropyl silane, trimethoxy mercaptopropyl silane, methyl dimethoxy mercaptopropyl silane, methyl diethoxy mercaptopropyl silane, dimethyl methoxy mercaptopropyl silane, triethoxy mercaptoethyl silane, tripropoxy mercaptopropyl silane, ethoxy dimethoxy mercaptopropylsilane, ethoxy diisopropoxy mercaptopropylsilane, ethoxy didodecyloxy mercaptopropylsilane and ethoxy dihexadecyloxy mercaptopropylsilane. Such organoalkoxymercaptosilanes may be capped with a blocking group, i.e., the mercapto hydrogen atom is replaced with another group. A representative example of a capped organoalkoxymercaptosilane coupling agent is a liquid 3-octanoylthio-1-propyltriethoxysilane, commercially available as NXT™ Silane from Momentive Performance Materials Inc.

[0042] Mixtures of various organosilane polysulfide compounds and organoalkoxymercaptosilanes can be used.

[0043] The amount of coupling agent in the rubber composition is the amount needed to produce acceptable results, which is easily determined by one skilled in the art. The amount of coupling agent is typically based on the weight of the silica in the composition, and may be from about 0.1% to about 20% by weight of silica, from about 1% to about 15% by weight of silica, or alternatively from about 1% to about 10% by weight of silica.

[0044] Other ingredients that may be added to the rubber composition include, but are not limited to, oils, waxes, scorch inhibiting agents, tackifying resins, reinforcing resins, fatty acids such as stearic acid, and peptizers. These ingredients are known in the art, and may be added in appropriate amounts based on the desired physical and mechanical properties of the rubber composition.

[0045] A vulcanizing agent is added to the rubber composition. Suitable vulcanizing agents are known in the art, and may be added in appropriate amounts based on the desired physical, mechanical, and cure rate properties of the rubber composition. Examples of vulcanizing agents include sulfur and sulfur donating compounds. The amount of the vulcanizing agent used in the rubber composition may, in certain embodiments, be from about 0.1 to about 10 phr, or from about 1 to about 5 parts by weight per 100 phr.

[0046] At least one vulcanization accelerator is added to the rubber composition. The type of vulcanization accelerator is not particularly limited. Numerous accelerators are known in the art and include, but are not limited to, diphenyl guanidine

(DPG), tetramethylthiuram disulfide (TMTD), 4,4'-dithiodimorpholine (DTDM), tetrabutylthiuram disulfide (TBTD), benzothiazyl disulfide (MBTS), 2-(morpholinothio) benzothiazole (MBS), N-tert-butyl-2-benzothiazole sulfonamide (TBBS), N-cyclohexyl-2-benzothiazole sulfonamide (CBS), and mixtures thereof. The total amount of vulcanization accelerator(s) used in the rubber composition may be from about 0.1 to about 10 phr or from about 1 to about 5 phr.

[0047] The rubber composition may be formed by mixing the ingredients together by methods known in the art, such as, for example, by kneading the ingredients together in a Banbury mixer.

[0048] As mentioned herein above, the rubber composition is formed by mixing the ingredients together in at least two mixing steps: at least one preparatory mixing step and a final mixing step. A preparatory mixing step is one in which no vulcanization agent, such as sulfur, is added. In the preparatory mixing step(s), the ingredients may be mixed to a temperature of about 140° C. to about 190° C., or to a temperature of about 150° C. to about 180° C. , or alternatively to a temperature of about 160° C. to about 175° C. If more than one preparatory mixing step is utilized, the temperatures of the preparatory mixing steps may be the same or different.

[0049] A final mixing step is one in which a vulcanizing agent, such as sulfur, is added. The final mixing step may be mixed to a temperature below the vulcanization temperature in order to avoid unwanted pre-cure of the rubber composition. Therefore, the temperature of the productive mixing stage should not exceed about 120° C. and is typically about 40° C. to about 120° C., or about 60° C. to about 110° C. and, especially, about 75° C. to about 100° C.

[0050] The composition is preferably allowed to cool to a temperature of 50° C. or lower between individual mixing steps.

[0051] One aspect of this disclosure is the fact that at least one vulcanization accelerator is added to the rubber composition during a preparatory mixing step, and no vulcanization accelerator is added during the final mixing step. In other words, all of the vulcanization accelerators are added to the rubber composition during a preparatory mixing step.

[0052] The preparatory mixing step in which the vulcanization accelerator(s) is added may be the same mixing step in which the polymer(s), silica, silica coupling agent, oil(s), and other ingredients are added. In one embodiment, the preparatory mixing step containing the vulcanization accelerator(s) is a mixing step in which only a vulcanization accelerator is added, and is conducted after all polymer(s), silica, and silica coupling agent has been added. In another embodiment, all processing aids, stearic acid, and antidegredants such as N-(1, 3-dimethylbutyl)-N'-phenyl-p-phenylene-diamine (6PPD), are added in a subsequent mixing stage to the preparatory mixing stage containing the vulcanization accelerator(s). The vulcanization accelerator(s) may optionally be added in more than one preparatory mixing step.

[0053] Without intending to be bound by theory, it is believed that the addition of a vulcanization accelerator in a preparatory mixing stage catalyzes the silanization reaction between the silica coupling agent and the rubbery polymer. It has unexpectedly been found that adding all of the accelerators of the rubber composition during a preparatory mixing step provides for reduced E' while maintaining approximately equal tangent delta. Thus, if the rubber composition is used as a tire tread composition, the snow traction of the tread may be improved by the method of this disclosure.

[0054] The rubber composition formed according to the disclosure herein is particularly useful as a tire tread rubber composition. However, in certain embodiments, it may be used as another tire component, such as a sidewall, bead filler, undertread, or a coating for a carcass ply. Additionally, other rubber articles may be formed from the rubber composition of the disclosure, such as an air spring component.

[0055] The present disclosure will be described in more detail with reference to the following examples. The following examples are presented for purposes of illustration only and are not to be construed in a limiting sense.

EXAMPLES

[0056] Five rubber compositions, Samples A-E, were prepared from the ingredients shown in Table 1. All amounts shown are in phr. Each of the compositions was mixed in four mixing steps in a Banbury type mixer—three preparatory mixing steps and a final mixing step. The ingredients in each preparatory mixing step were mixed to a temperature of about 175° C. before being dropped from the mixer, while the ingredients in the final mixing step were mixed to a temperature of about 110° C. before being dropped from the mixer.

TABLE 1

	Sample A	Sample B	Sample C	Sample D	Sample E
First Preparatory Mixing Step					
SBR	50	50	50	50	50
High Cis BR	40	40	40	40	40
Natural Rubber	10	10	10	10	10
Silica	45	45	45	45	45
Carbon Black	15	15	15	15	15
3,3'-bis(triethoxysilylpropyl)disulfide	3.96	3.96	3.96	3.96	3.96
Oil	31.75	31.75	31.75	31.75	31.75
6PPD	1.18	1.18	1.18	1.18	1.18
Wax	1.5	1.5	1.5	1.5	1.5
Stearic Acid	2	2	2	2	2
Zinc Oxide	2.5	2.5	2.5	2.5	2.5
Processing Additive (EF44A from Struktol)	2	2	2	2	2
Second Preparatory Mixing Step					
Silica	15	15	15	15	15
3,3'-bis(triethoxysilylpropyl)disulfide	1.32	1.32	1.32	1.32	1.32

TABLE 1-continued

	Sample A	Sample B	Sample C	Sample D	Sample E
Third Preparatory Mixing Step					
2,2'-Dithiobis(benzothiazole)	0	0	0.7	0.35	0.7
N-tert-Butyl-2-benzothiazolesulfenamide	0	0.7	0	0.35	0.7
N,N'-Diphenylguanidine	1.35	1.35	1.35	1.35	1.35
Final Mixing Step					
Sulfur	1.85	1.85	1.85	1.85	1.85
Processing Additive (Struktol WB212)	3	3	3	3	3
N-tert-Butyl-2-benzothiazolesulfenamide	0.7	0	0.7	0.35	0
2,2'-Dithiobis(benzothiazole)	0.7	0.7	0	0.35	0

[0057] Indexing the results to those of Sample A, the rubber compositions had the properties shown in Table 2. Dynamic viscoelastic mechanical property determinations for E' and tangent delta were made by temperature sweep tests conducted at a frequency of 52 Hz using 0.2% strain for temperatures from −50° C. to −6° C. and using 1.0% strain for temperatures from −5° C. to 60° C. The specimens used for dynamic viscoelastic testing were cured for 15 minutes at 170° C., and had the following dimensions: 40 mm long, 4.7 mm wide, and 2 mm thick.

TABLE 2

	A	B	C	D	E
E' @ −20° C. (MPa)	100	99	92	102	84
E' @ 0° C. (MPa)	100	100	93	103	88
Tangent Delta @ 0° C.	100	99	99	101	97
E' @ 30° C. (MPa)	100	102	94	104	90
Tangent Delta @ 30° C.	100	101	95	100	95
E' @ 60° C. (MPa)	100	103	95	104	91
Tangent Delta @ 60° C.	100	101	94	98	97

[0058] As can be seen from Table 2, the addition of all the vulcanization accelerators in a preparatory mixing step unexpectedly has a much larger affect on lowering the E', especially the E'@−20° C. If the rubber composition is used as a tire tread, lower E'@−20° C. is indicative of improved snow traction.

[0059] The description has been provided with exemplary embodiments. Modifications and alterations may occur to others upon reading and understanding the preceding detailed description. It is intended that the disclosure and exemplary embodiments be construed as including all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.

What is claimed is:

1-16. (canceled)

17. A method of preparing a rubber composition comprising:

- a. blending in at least one preparatory mixing step
  - (i) at least one natural or synthetic rubbery polymer,
  - (ii) a silica filler,
  - (iii) a silica coupling agent, and
  - (iv) at least one vulcanization accelerator; and
- b. subsequently blending therewith in a final mixing step a sulfur curative, wherein the final mixing step is void of any vulcanization accelerator.

18. The method of claim **17**, wherein the at least one vulcanization accelerator is used in an amount of about 0.1 to about 10 phr.

19. The method of claim **17**, wherein

the at least one natural or synthetic rubbery polymer is selected from the group consisting of natural rubber, synthetic polyisoprene rubber, styrene-butadiene rubber (SBR), styrene-isoprene rubber, styrene-isoprene-butadiene rubber, butadiene-isoprene-styrene terpolymer, butadiene-isoprene rubber, polybutadiene rubber, neoprene, and mixtures thereof; and

the silica coupling agent is selected from the group consisting of organosulfide polysulfides, organoalkoxymercaptosilanes, capped organoalkoxymercaptosilanes, and mixtures thereof.

20. The method of claim **17**, wherein the at least one natural or synthetic rubbery polymer is selected from the group consisting of styrene-butadiene rubber, polybutadiene rubber, and mixtures thereof.

21. The method of claim **17**, wherein the silica coupling agent is 3,3'-bis(triethoxysilylpropyl)disulfide.

22. The method of claim **17**, wherein the at least one vulcanization accelerator is guanidine-based, thiocarbamate-based, thiuram sulfide-based, or benzothiazole-based.

23. The method of claim **17**, wherein the at least one vulcanization accelerator is selected from the group consisting of: 1,3-diphenyl guanidine (DPG), tetramethylthiuram disulfide (TMTD), 4,4'-dithiodimorpholine (DTDM), tetrabutylthiuram disulfide (TBTD), benzothiazyl disulfide (MBTS), 2-(morpholinothio) benzothiazole (MBS), N-tert-butyl-2-benzothiazole sulfonamide (TBBS), N-cyclohexyl-2-benzothiazole sulfonamide (CBS), and mixtures thereof.

24. The method of claim **17**, wherein the at least one vulcanization accelerator is added in a mixing step separately from other materials and after addition of all filler, rubbery polymer, and silica coupling agent.

25. The method of claim **17**, wherein the preparatory mixing step containing the vulcanization accelerator is mixed to a temperature of about 140° C. to about 190° C.

26. The method of claim **17**, wherein the at least one vulcanization accelerator is 1,3-diphenylguanidine.

27. The method claim **17**, wherein the at least one preparatory mixing stage further comprises carbon black.

28. The method of claim **17**, wherein the silica filler is present in an amount of 5 to 80 phr.

29. The method of claim **17**, wherein the blending of (a) further comprises carbon black in an amount of 5 to 100 phr.

30. The method of claim **29**, wherein the silica filler and carbon black are present at a ratio (based on phr) of 1:1 to 10:1.

31. The method of claim **1**, wherein the at least one vulcanization accelerator is added in a second preparatory mixing step separately from other materials and after addition of (i), (ii), (iii).

32. The method of claim **1**, wherein the rubber composition includes one or more of: (v) processing aid(s), (vi) fatty acid(s), and (vii) antidegradant(s), and (v), (vi) and (vii) are added in a subsequent mixing stage to the preparatory mixing stage containing the at least one vulcanization accelerator.

33. A method of preparing a rubber composition comprising:

blending in at least one preparatory mixing step:

at least one natural or synthetic rubbery polymer selected from the group consisting of natural rubber, synthetic polyisoprene rubber, styrene-butadiene rubber (SBR), styrene-isoprene rubber, styrene-isoprene-butadiene rubber, butadiene-isoprene-styrene terpolymer, butadiene-isoprene rubber, polybutadiene rubber, neoprene, and mixtures thereof, a silica filler and up to 100 phr of carbon black filler, and a silica coupling agent, and

then mixing about 0.1 to about 10 phr at least one vulcanization accelerator in a mixing step separately from other materials and after addition of all filler, rubbery polymer, and silica coupling agent; and

subsequently blending therewith in a final mixing step a sulfur curative, wherein the final mixing step is void of any vulcanization accelerator.

34. The method of claim **33**, wherein the at least one vulcanization accelerator is guanidine-based, thiocarbamate-based, thiuram sulfide-based, or benzothiazole-based.

35. A method of preparing a rubber composition comprising:

blending in at least one preparatory mixing step:

at least one natural or synthetic rubbery polymer selected from the group consisting of natural rubber, synthetic polyisoprene rubber, styrene-butadiene rubber (SBR), styrene-isoprene rubber, styrene-isoprene-butadiene rubber, butadiene-isoprene-styrene terpolymer, butadiene-isoprene rubber, polybutadiene rubber, neoprene, and mixtures thereof,

a silica filler and up to 100 phr of carbon black filler, and

a silica coupling agent, and

then mixing about 0.1 to about 10 phr of at least one vulcanization accelerator including 1,3-diphenyl guanidine in a mixing step separately from other materials and after addition of all filler, rubbery polymer, and silica coupling agent; and

subsequently blending therewith in a final mixing step a sulfur curative, wherein the final mixing step is void of any vulcanization accelerator.

36. A rubber composition produced by the method claim **17**.

* * * * *