



(86) Date de dépôt PCT/PCT Filing Date: 1999/11/24

(87) Date publication PCT/PCT Publication Date: 2000/06/08

(45) Date de délivrance/Issue Date: 2009/03/17

(85) Entrée phase nationale/National Entry: 2001/05/31

(86) N° demande PCT/PCT Application No.: US 1999/027890

(87) N° publication PCT/PCT Publication No.: 2000/032684

(30) Priorité/Priority: 1998/12/01 (US09/203,438)

(51) Cl.Int./Int.Cl. *C08J 3/20* (2006.01),
B60C 1/00 (2006.01), *C08J 5/10* (2006.01),
C08K 3/36 (2006.01), *C08K 5/1535* (2006.01),
C08K 5/5419 (2006.01), *C08L 21/00* (2006.01)

(72) Inventeurs/Inventors:
HERGENROTHER, WILLIAM L., US;
HILTON, ASHLEY S., US;
COLE, WILLIAM M., US;
OZIOMEK, JAMES, US

(73) Propriétaire/Owner:
BRIDGESTONE CORPORATION, JP

(74) Agent: OGILVY RENAULT LLP/S.E.N.C.R.L.,S.R.L.

(54) Titre : APTITUDE AU TRAITEMENT AMELIOREE DE MASSES DE CAOUTCHOUC CHARGEES DE SILICE

(54) Title: IMPROVED PROCESSABILITY OF SILICA-FILLED RUBBER STOCKS

(57) **Abrégé/Abstract:**

The present invention provides silica-filled, vulcanized elastomeric compounds comprising an elastomer mixed with at least a silica filler, a processing aid, and a curing agent, and processes for the preparation of the same. Generally, the present invention provides processing aids which effectively reduces or replace the amount (i.e., about 10 percent by weight based upon the silica filler) of the processing aid bis [3-triethoxysilyl)propyl]tetrasulfide ("Si69") used in the production of silica-filled rubber stocks. These new processing aids include alkyl alkoxysilanes, fatty acid esters of hydrogenated and non-hydrogenated sugars and the polyoxyethylene derivatives thereof, and combinations thereof, with or without various non-reinforcing fillers such as mineral fillers. The processing aids do not hinder the physical properties of the compounds and have been found to be excellent substitutes for Si69. The processing aids may be supported on the silica filler or any of the other fillers employed in the composition for improved handling, safety and performance. Processes for the preparation of the silica filled vulcanizable elastomers are provided as well as pneumatic tires employing tread stock comprising the novel vulcanizable elastomers.

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08K 5/00, 3/36, 9/12, C08L 21/00	A1	(11) International Publication Number: WO 00/32684 (43) International Publication Date: 8 June 2000 (08.06.00)
(21) International Application Number: PCT/US99/27890 (22) International Filing Date: 24 November 1999 (24.11.99) (30) Priority Data: 09/203,438 1 December 1998 (01.12.98) US (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 09/203,438 (CON) Filed on 1 December 1998 (01.12.98) (71) Applicant (for all designated States except US): BRIDGE-STONE CORPORATION [JP/JP]; 10-1, Kyobashi 1-chome, Chuo-ku, Tokyo 104 (JP). (72) Inventors; and (75) Inventors/Applicants (for US only): HERGENROTHER, William, L. [US/US]; 195 Dorchester Road, Akron, OH 44313 (US). HILTON, Ashley, S. [US/US]; 7431 Shadeview, NW, Massillon, OH 44646 (US). COLE, William, M. [US/US]; 6595 Fairland Road, Clinton, OH 44216 (US). OZIOMEK, James [US/US]; 1834 Calvert Drive, Cuyahoga Falls, OH 44223 (US).		(74) Agents: HORNICKEl, John et al.; Bridgestone/Firestone, Inc., 1200 Firestone Parkway, Akron, OH 44317-0001 (US). (81) Designated States: CA, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: IMPROVED PROCESSABILITY OF SILICA-FILLED RUBBER STOCKS (57) Abstract <p>The present invention provides silica-filled, vulcanized elastomeric compounds comprising an elastomer mixed with at least a silica filler, a processing aid, and a curing agent, and processes for the preparation of the same. Generally, the present invention provides processing aids which effectively reduces or replace the amount (i.e., about 10 percent by weight based upon the silica filler) of the processing aid bis [3-triethoxysilyl)propyl]tetrasulfide ("Si69") used in the production of silica-filled rubber stocks. These new processing aids include alkyl alkoxysilanes, fatty acid esters of hydrogenated and non-hydrogenated sugars and the polyoxyethylene derivatives thereof, and combinations thereof, with or without various non-reinforcing fillers such as mineral fillers. The processing aids do not hinder the physical properties of the compounds and have been found to be excellent substitutes for Si69. The processing aids may be supported on the silica filler or any of the other fillers employed in the composition for improved handling, safety and performance. Processes for the preparation of the silica filled vulcanizable elastomers are provided as well as pneumatic tires employing tread stock comprising the novel vulcanizable elastomers.</p>		

IMPROVED PROCESSABILITY OF SILICA-FILLED RUBBER STOCKS

5

Field of the Invention

The present invention relates to the processing and vulcanization of diene polymer and copolymer elastomer-containing rubber stocks and, more particularly, silica-filled rubber stocks using processing aids with or without other reinforcing fillers.

10

Background of the Invention

In the art it is desirable to produce elastomeric compounds exhibiting reduced hysteresis when properly compounded with other ingredients such as reinforcing agents, followed by vulcanization. Such elastomers, when compounded, fabricated and vulcanized into components for constructing articles such as tires, power belts, and the like, will manifest properties of increased rebound, decreased rolling resistance and less heat-build up when subjected to mechanical stress during normal use.

15

The hysteresis of an elastomer refers to the difference between the energy applied to deform an article made from the elastomer and the energy released as the elastomer returns to its initial, undeformed state. In pneumatic tires, lowered hysteresis properties are associated with reduced rolling resistance and heat build-up during operation of the tire. These properties, in turn, result in lower fuel consumption for vehicles using such tires.

20

25

In such contexts, the property of lowered hysteresis of compounded, vulcanizable elastomer compositions is particularly significant. Examples of such compounded elastomer systems are known to the art and typically include at least one elastomer (that is, a natural or synthetic polymer exhibiting elastomeric properties, such as a rubber), a reinforcing (or non-reinforcing) filler agent (such as finely divided carbon black, thermal black, or mineral fillers such as clay and the like) and a vulcanizing system such as a sulfur-containing vulcanizing (i.e., curing) system.

30

Recently, precipitated silica has been increasingly used as a reinforcing particulate filler in carbon black-filled rubber components of tires and mechanical goods. While providing excellent properties, including reduced hysteresis, to the rubber stocks, these silica-loaded rubber stocks are
5 unfortunately not easily produced, exhibiting relatively poor processability characteristics.

Summary of the Invention

Other work has resulted in improvements in processing
10 characteristics for silica-loaded rubber stocks, particularly that work disclosed in European Patent Publications EP 0 890 603A1 and EP 0 890 606A1. This invention carries forward such work.

The present invention provides reinforcing filler-supported additives, such as a mineral fillers, capable of improving the processability of
15 the formulations of diene polymer elastomers reinforced with silica filler.

The present invention also provides a process for decreasing the level of bis[3-(triethoxysilyl)propyl]tetrasulfide (Si69) in silica-filled elastomeric vulcanizable compounds.

The present invention also provides vulcanizable silica-filled
20 elastomeric compounds having enhanced physical properties, including decreased hysteresis and increased tear strength.

One aspect of the invention is a process for the preparation of a silica-filled, vulcanized elastomeric compound comprising: (a) mixing (1) 100 parts by weight of an elastomer; (2) from about 5 to about 100 parts by weight
25 of a reinforcing filler selected from the group consisting of silica filler or mixtures thereof with carbon black, per 100 parts of said elastomer; (3) from about 0.1 to about 150 percent by weight, based on said silica filler, of a processing aid selected from the group consisting of alkylalkoxysilanes, fatty acid esters of hydrogenated and non-hydrogenated C₅ and C₆ sugars;
30 polyoxyethylene derivatives of fatty acid esters of hydrogenated and non-hydrogenated C₅ and C₆ sugars and mixtures thereof; (4) optionally from 0 to about 40 parts by weight of a non-reinforcing filler, per 100 parts elastomer,

with the provisos that if said processing aid is sorbitan monooleate, then at least one of said polyoxyethylene derivatives or said additional fillers is also present and, that the minimal amount for each said processing aid and said additional filler, if present, is about one part by weight; (5) optionally from 0 to about 20 percent by weight of bis[3-(triethoxysilyl)propyl]tetrasulfide, based upon the weight of said silica filler; and (6) a cure agent; wherein, optionally, said processing aid is first mixed with and supported on at least some of either said reinforcing filler or said non-reinforcing filler prior to mixing with said elastomer; and (b) effecting vulcanization.

Another aspect of the invention is a vulcanizable, silica-filled compound comprising: 100 parts by weight of an elastomer; from about 5 to about 100 parts by weight of a reinforcing filler selected from the group consisting of silica filler or mixtures thereof with carbon black, per 100 parts of said elastomer; optionally from 0 to about 20 percent by weight of bis[3-(triethoxysilyl)propyl]tetrasulfide, based upon the weight of said silica filler; from about 0.1 to about 150 percent by weight, based on said silica filler, of a processing aid selected from the group consisting of alkylalkoxysilanes, fatty acid esters of hydrogenated and non-hydrogenated C₅ and C₆ sugars; polyoxyethylene derivatives of fatty acid esters of hydrogenated and non-hydrogenated C₅ and C₆ sugars and mixtures thereof; optionally from 0 to about 40 parts by weight of a non-reinforcing filler, per 100 parts elastomer; and a cure agent; wherein, optionally, said processing aid is supported on at least some of either said reinforcing filler or said optional non-reinforcing filler; and with the provisos that if said processing aid is sorbitan monooleate, then at least one of said polyoxyethylene derivatives or said additional fillers is also present and, that the minimal amount for each said processing aid and said additional filler, if present, is about one part by weight.

Another aspect of the invention is a pneumatic tire comprising tread stock vulcanized from the above vulcanizable silica-filled compound.

Another aspect of the invention is a pneumatic tire comprising tread stock obtainable from the above inventive process.

A further aspect of the invention is a process for the preparation of a silica-filled, vulcanized elastomeric compound comprising:

- (a) mixing
 - (1) 100 parts by weight of an elastomer;
 - 5 ○ (2) from 5 to 100 parts by weight of a reinforcing filler selected from the group consisting of silica filler or mixtures thereof with carbon black, per 100 parts of said elastomer, wherein the silica filler has a BET surface area of 150 to 220m²/g;
 - 10 ○ (3) from 0.1 to 150 percent by weight, based on said silica filler, of a combination of an alkylalkoxysilane and an additional processing aid selected from the group consisting of fatty acid esters of hydrogenated and non-hydrogenated C₅ and C₆ sugars, polyoxyethylene derivatives of fatty acid esters of hydrogenated and non-hydrogenated C₅ and C₆ sugars and mixtures thereof;
 - 15 ○ (4) optionally from 0 to 40 parts by weight of a non-reinforcing filler, per 100 parts elastomer;
 - (5) optionally from 0 to 20 percent by weight of bis[(triethoxysilyl)-propyl]tetrasulfide, based upon the weight of said silica filler; and
 - 20 ○ (6) a cure agent;

wherein said alkylalkoxysilane and said additional processing aid are first mixed with and supported on at least some of either said silica reinforcing filler or said non-reinforcing filler prior to mixing with said elastomer,

and wherein the minimal amount for the alkylalkoxysilane and said
25 additional processing aid is about one part by weight; and

- (b) effecting vulcanization.

Embodiments of the Invention

One skilled in the art is directed to the disclosures of European Patent Publications EP 0 890 603A1 and EP 0 890 606A1, wherein one can find
5 full explanations of the work upon which this invention is built. Because of the availability of such publications, the text of those disclosures is not repeated here but is relied upon.

Examples of this invention are provided below, with brief explanations of the embodiments of this invention that emphasize the points of
10 departure from the disclosures of European Patent Publications EP 0 890 603A1 and EP 0 890 606A1.

In one embodiment, the present invention provides a silica-filled, vulcanizable elastomeric compound useful as tread stocks for pneumatic tires that employs a processing aid as a replacement for Si69, wherein the
15 processing aid is selected from the group consisting of alkyl alkoxysilanes, fatty acid esters of hydrogenated and non-hydrogenated sugars, ethoxylated derivatives of fatty acid esters of hydrogenated and non-hydrogenated sugars, and mixtures thereof and wherein the processing aid is supported on the silica filler or other filler, e.g., either another reinforcing filler such as carbon black,
20 or a non-reinforcing filler such as one of a number of mineral fillers or the like.

In another embodiment, from about 0.1 to about 150 percent by weight of an alkyl alkoxysilane is used in the present invention as a processing aid. Thus, given the amount of silica filler typically preferred in the subject composition, up to about 150 parts by weight of the processing aid, per 100
25 parts elastomer, may be used, representing a 60/40 ratio of processing aid to silica.

In yet another embodiment, a mixture of a filler and a filler-supported processing aid selected from the group consisting of alkyl alkoxysilanes, fatty acid esters of hydrogenated and non-hydrogenated sugars,
30 ethoxylated derivatives of fatty acid esters of hydrogenated and non-hydrogenated sugars, and mixtures thereof, is preferably added to the elastomer in an amount of about 5 to about 100 parts by weight per 100 parts of the

elastomer. It should be stressed that when a silica-supported or carbon black-supported processing aid is used, the non-reinforcing fillers, including mineral fillers or other processing aids are not required in the elastomeric formulation. However, it will be appreciated that if mineral fillers are used, they may be used
5 to support the processing aid(s). Preferably, the processing aid is added to the silica or other filler in a mixture ratio of from about 1:99 to about 60:40, with a 50:50 mixture being most preferred.

In yet another embodiment, certain additional fillers can be utilized according to the present invention as processing aids which include, but
10 are not limited to, mineral fillers, such as clay (hydrous aluminum silicate), talc (hydrous magnesium silicate), and mica as well as non-mineral fillers such as urea and sodium sulfate. Preferred micas contain principally alumina, silica and potash, although other variants are also useful, as set forth below. The additional fillers are also optional and can be utilized in the amount of from 0
15 parts to about 40 parts per 100 parts of polymer (phr), preferably in an amount from about 1 to about 20 phr. It will be understood that these mineral fillers can also be used as non-reinforcing fillers to support the processing aids of the present invention.

Thus, a process for the preparation of a silica-filled, vulcanized
20 elastomeric compound according to the present invention comprises mixing an elastomer with from about 5 to about 100 parts by weight of a reinforcing filler selected from the group consisting of silica filler and mixtures thereof with carbon black, from 0 to about 20 percent by weight, based on said silica filler, of bis[3-(triethoxysilyl)propyl]tetrasulfide, from 0.1 to about 150 percent by
25 weight, based on said silica filler, of an alkylalkoxysilane, and a cure agent; and, effecting vulcanization.

Further, the present invention also includes a vulcanizable silica-filled compound comprising an elastomer, a silica filler, from 0 to about 20 percent by weight, based on said silica filler, of bis[3-
30 (triethoxysilyl)propyl]tetrasulfide, from about 0.1 to about 150 percent by

weight, based on said silica filler, of an alkylalkoxysilane, and a cure agent. Preferably, the compound further contains a natural rubber.

Further, the present invention also includes a pneumatic tire comprising tread stock vulcanized from the above compound made from the
5 above process.

The elastomer can be a diene monomer homopolymer or a copolymer of a diene monomer and a monomer selected from the group consisting of monovinyl aromatic monomers and triene monomers.

The alkylalkoxysilane can be represented by the formula
10 $(R_1)_2Si(OR_2)_2$ or $R_1Si(OR_2)_3$, wherein each R_1 independently is selected from the group consisting of C_1 to about C_{18} aliphatic, about C_5 to about C_{12} cycloaliphatic, and about C_6 to about C_{18} aromatic; and wherein the alkoxy groups are the same or are different, each R_2 independently containing from one to about 6 carbon atoms.

15 The alkylalkoxysilane can be selected from the group consisting of octyltriethoxy silane, octyltrimethyloxy silane, (3-glycidoxypentyl)trimethoxy silane, (3-glycidoxypentyl)triethoxy silane, hexyltrimethoxy silane, ethyltrimethoxy silane, propyltriethoxy silane, phenyltrimethoxy silane, cyclohexyltrimethoxy silane, cyclohexyltriethoxy
20 silane, dimethyldimethoxy silane, 3-chloropentyltriethoxy silane, methacryltrimethoxy silane, and i-butyltriethoxy silane. Preferably, the alkylalkoxysilane is octyltriethoxysilane.

In one option for the above process, one can mix, prior to the vulcanizing step, a processing aid comprising at least one of an ester of a fatty
25 acid or an ester of a polyol. Preferably, that processing aid is selected from the group consisting of at least one sorbitan ester of an oleate, laurate, palmitate and stearate fatty acids, polyoxyethylene derivatives thereof, at least one ester of a polyhydroxy compound, and mixtures thereof. More preferably, that processing aid is sorbitan monooleate.

30 Preferably for the above process, the elastomer is a styrene butadiene rubber. More preferably, the elastomer is a copolymer of styrene

butadiene rubber and butyl rubber. Even more preferably, the elastomer is mixed with carbon black.

The process also optionally includes mixing insoluble sulfur prior to the vulcanizing step.

5 The present invention also includes a first alternative process for the preparation of a silica-filled, vulcanized elastomeric compound comprising the steps of

mixing an elastomer with from about 5 to about 100 parts by weight of a reinforcing filler per 100 parts of elastomer, wherein said reinforcing fillers are

10 selected from the group consisting of silica filler and mixtures thereof with carbon black; from 0 to about 20 percent by weight of bis[3-(triethoxysilyl)propyl]tetrasulfide, based upon the weight of said silica filler;

from about 0.1 to about 150 percent by weight of a processing aid selected from the group consisting of fatty acid esters of hydrogenated and non-hydrogenated

15 C₅ and C₆ sugars, polyoxyethylene derivatives of fatty acid esters of hydrogenated and non-hydrogenated C₅ and C₆ sugars, and mixtures thereof;

from about 0 to about 40 parts by weight of an additional filler other than silica or carbon black, with the provisos that if said processing aid is sorbitan monooleate, then at least one of said polyoxyethylene derivatives or said

20 additional fillers is also present and, that the minimal amount for each said processing aid and said additional filler, if present, is about one part by weight; and a cure agent; and effecting vulcanization.

The first alternative process utilizes a vulcanizable silica-filled compound which comprises 100 parts by weight of an elastomer; from about 5

25 to about 100 parts by weight of a reinforcing filler per 100 parts of elastomer, wherein said reinforcing fillers are selected from the group consisting of silica filler and mixtures thereof with carbon black; from 0 to about 20 percent by weight of bis[3-(triethoxysilyl)propyl]tetrasulfide, based upon the weight of said silica filler; from about 0.1 to about 150 percent by weight of a processing

30 aid selected from the group consisting of fatty acid esters of hydrogenated and non-hydrogenated C₅ and C₆ sugars, polyoxyethylene derivatives of fatty acid

esters of hydrogenated and non-hydrogenated C₅ and C₆ sugars, and mixtures thereof; from about 0 to about 40 parts by weight of an additional filler other than silica or carbon black; and a cure agent; with the provisos that if said processing aid is sorbitan monooleate, then at least one of said polyoxyethylene derivatives or said additional fillers is also present and, that the minimal amount for each said processing aid and said additional filler, if present, is about one part by weight.

Further, the present invention also includes a pneumatic tire comprising tread stock vulcanized from the above alternative compound made from the above alternative process.

The alternative process and vulcanizable compound are utilize the same preferences of process steps and ingredients, except as noted below.

The alternative process can include an additional step of adding a natural rubber.

Preferably, silica filler used in the alternative process and compound has a surface area of about 32 to about 400 m²/g and a pH of about 5.5 to about 7.

Preferably, the alternative process and compound has an amount of said carbon black reinforcing filler ranging from about 0 to about 50 parts by weight, per 100 parts by weight of elastomer, and an amount of said reinforcing silica filler ranging from about 1 to 100 parts, per 100 parts of elastomer, with the proviso that where carbon is 0, at least 30 phr of silica is employed.

Preferably, the fatty acid esters of hydrogenated and non-hydrogenated C₅ and C₆ sugars are selected from the group consisting of sorbitan monooleate, sorbitan dioleate, sorbitan trioleate, sorbitan sesquioleate, sorbitan laurate, sorbitan palmitate and sorbitan stearate, while the polyoxyethylene derivatives of fatty acid esters of hydrogenated and non-hydrogenated C₅ and C₆ sugars are selected from the group consisting of POE (20) sorbitan stearate; POE (20) sorbitan oleate; POE (20) sorbitan tri-oleate; POE (20) sorbitan sesquioleate; POE (20) sorbitan laurate and POE (20) sorbitan palmitate. More preferably, the processing aid comprises a mixture of

at least one fatty acid ester of hydrogenated and non-hydrogenated C₅ and C₆ sugars and at least one polyoxyethylene derivative of a fatty acid ester of hydrogenated and non-hydrogenated C₅ and C₆ sugars.

Preferably, the additional filler is selected from the group
5 consisting of mica, talc, urea, clay, sodium sulfate and mixtures thereof and more preferably, is included with the mixture of at least one fatty acid ester of hydrogenated and non-hydrogenated C₅ and C₆ sugars.

The present invention provides a second alternative process for
10 the preparation of a silica-filled, vulcanized elastomeric compound comprising mixing 100 parts by weight of an elastomer with from about 5 to about 100 parts by weight of a reinforcing filler selected from the group consisting of silica filler or mixtures thereof with carbon black, per 100 parts of said elastomer; from about 0.1 to about 150 percent by weight, based on said silica
15 filler, of a processing aid selected from the group consisting of alkylalkoxysilanes, fatty acid esters of hydrogenated and non-hydrogenated C₅ and C₆ sugars; polyoxyethylene derivatives of fatty acid esters of hydrogenated and non-hydrogenated C₅ and C₆ sugars and mixtures thereof; from 0 to about 40 parts by weight of a non-reinforcing filler, per 100 parts elastomer; and a
20 cure agent; wherein said processing aid is first mixed with and supported on at least some of either said reinforcing filler or said non-reinforcing filler prior to mixing with said elastomer; and effecting vulcanization.

The second alternative process utilizes a vulcanizable, silica-filled compound comprising 100 parts by weight of an elastomer; from about 5
25 to about 100 parts by weight of a reinforcing filler selected from the group consisting of silica filler or mixtures thereof with carbon black, per 100 parts of said elastomer; from about 0.1 to about 150 percent by weight, based on said silica filler. of a processing aid selected from the group consisting of alkylalkoxysilanes, fatty acid esters of hydrogenated and non-hydrogenated C₅
30 and C₆ sugars; polyoxyethylene derivatives of fatty acid esters of hydrogenated and non-hydrogenated C₅ and C₆ sugars and mixtures thereof; from 0 to about

40 parts by weight of a non-reinforcing filler, per 100 parts elastomer; and a cure agent; wherein said processing aid is supported on at least some of either said reinforcing filler or said non-reinforcing filler.

Further, the present invention also includes a pneumatic tire
5 comprising tread stock vulcanized from the above second alternative compound made from the above second alternative process.

The second alternative process and vulcanizable compound are utilize the same preferences of process steps and ingredients as the first alternative process and vulcanizable compound, except as noted below.

10 As with the initial process and vulcanizable compound described above, the alkyl alkoxysilanes are selected from the group consisting of octyltriethoxy silane, octyltrimethoxy silane, (3-glycidoxypropyl)trimethoxy silane, (3-glycidoxypropyl)triethoxy silane, hexyltrimethoxy silane, ethyltrimethoxy silane, propyltriethoxy silane, phenyltrimethoxy silane,
15 cyclohexyltrimethoxy silane, cyclohexyltriethoxy silane, dimethyldimethoxy silane, 3-chloropropyltriethoxy silane, methacroyltrimethoxy silane, and i-butyltriethoxy silane.

Preferably, for the second alternative vulcanizable silica-filled compound, the silica or carbon black-support processing aid is provided as a
20 50/50 mixture of processing aid to support.

The following examples amplify upon these embodiments.

Examples

Testing of silica-filled vulcanizable elastomeric compounds was
25 conducted to determine the effect silica-supported and carbon black-supported alkyl alkoxysilanes and polyoxyethylene derivatives of fatty acid esters of hydrogenated and non-hydrogenated sugars as processing aids in the elastomeric stock formulations. The basic formulation, C-CC, of the elastomeric stock formulation is shown and described in Table I below.

30 The physical properties of the Example Nos. 1-6 and the control, C-DD, are shown and described in Table II, below. Example Nos. 2-6 indicated

- a Mooney viscosities (ML 1+4/100°C) comparable to the control, C-DD, with 3 phr of Si69 processing aid. Tensile properties of the cured elastomeric stocks, containing processing aids comprising octyl triethoxy silane and sorbitan oleate supported on silica are comparable to the tensile properties of the control elastomeric stock formulation, C-DD, containing 3 phr of Si69 processing aid. Curing at 171°C for 20 minutes was used to obtain the physical properties set forth below.

TABLE I	
Basic Formulation of Elastomeric Stock (C-CC)	
Component	Parts
SBR	75
NR	25
Oil	15
carbon black	35
silica	VARIABLE
stearic acid	1.5
wax	1.0
process aid	VARIABLE
antioxidant	0.95
sulfur	1.7
CBS	1.5
DPG	0.5
Zinc oxide	2.5

10

Table I Continued							
Final Elastomeric Stock Formulations Examples C-DD and 1-6							
Example	C-DD	1	2	3	4	5	6
46% SO on Silica ^a	C	3.3	3.3	---	---	---	---

WO 00/32684

PCT/US99/27890

Table I Continued							
Final Elastomeric Stock Formulations Examples C-DD and 1-6							
Example	C-DD	1 *	2	3	4	5	6
47% OS on Silica ^b	---	1.5	2.5	---	---	---	---
5% SO/3.8% OS on Silica ^c	---	---	---	32.9	---	---	---
5% SO/3.8% OS on Silica ^d	---	---	---	---	32.9	---	---
Sorbitan Oleate (SO)	---	---	---	---	---	1.65	1.65
Octyl triethoxysilane (OS)	---	---	---	---	---	1.25	1.25

a Flogard SP (712-090)

b Flogard SP (712-091)

c Flogard SP (712-097)

d HiSil (712-098)

5

Table II							
Physical Properties of Elastomeric Formulations							
Example	C-DD	1	2	3	4	5	6
Mooney Viscosity							
ML 1+4/100°C	77.6	132.4	75.2	77.9	80.8	64.6	72.9
T80	9.7	43.5	7.5	8.5	9.3	6.5	7.4
MDR Monsanto Cure at 165°C							
ML	11.01	3.86	3.48	3.7	3.75	3.13	3.32
MH	35.37	20.42	19.39	19.67	20.28	18.89	19.1
ts2	2:36	2:08	2:16	2:26	2:16	2:22	2:24
tc90	17:06	13:55	11:14	10:37	11:14	10:41	10:02
tan δ at MH	---	0.144	0.145	0.158	0.15	0.134	0.135
Ring Tensile at 24°C							
50% Modulus, psi	221	256	230	209	219	207	227
100% Modulus, psi	322	403	360	331	356	331	360

* comparative

Table II Physical Properties of Elastomeric Formulations							
Example	C-DD	1	2	3	4	5	6
200% Modulus, psi	615	819	766	678	739	697	765
300% Modulus, psi	1008	1407	1338	1177	1279	1234	1335
Tensile Strength, psi	1852	2082	1899	1726	1959	1840	1886
% Elongation	474	400	386	392	407	395	381
Break energy, in-lbs/in ²	4012	3762	3229	3013	3549	3156	3166
Ring Tensile at 100°C							
50% Modulus,psi	189	229	208	212	196	193	190
100% Modulus, psi	263	350	323	312	303	296	300
200% Modulus, psi	518	685	654	632	607	614	604
300% Modulus, psi	869	1140	1107	1022	1025	1070	1023
Tensile Strength, psi	1299	1248	1227	1203	1075	1097	1148
% Elongation	412	322	322	327	310	308	326
Break energy, in-lbs/in ²	2496	1894	1837	1813	1557	1552	1761
Ring Tear at 171°C, psi	184.9	175.6	140.8	152.2	108.2	118.4	154
Wet Stanley London(#/std)	59/53	57/52	57/52	58/52	58/52	57/52	57/52
Shore A, at RT	----	72	70	67	67	67	66
Shore A at 50°C	----	67	67	65	67	66	65
Rheometrics at 7% Strain							
tan δ at 24°C	0.193	0.195	0.169	0.173	0.175	0.166	0.180
$\delta G' \times 10^{-7}$ at 24°C	4.239	4.506	4.879	5.267	4.718	3.94	4.712

Table II Physical Properties of Elastomeric Formulations							
Example	C-DD	1	2	3	4	5	6
24°C G' x 10 ⁻⁷ at 14.5%	3.006	3.138	3.261	3.01	3.127	2.856	3.422
tan δ at 65°C	0.152	0.153	0.155	0.143	0.145	0.138	0.149
δ G' x 10 ⁻⁷ at 65°C	2.689	3.779	5.667	3.939	4.554	4.172	3.836
50°C G' x 10 ⁻⁷ at 14.5%	2.42	2.736	2.77	2.731	2.992	2.509	2.6
Mr, g/mol from Tensile Retraction	13680	10440	----	11320	----	----	----

Further testing of silica-filled vulcanizable elastomeric stock formulations was conducted to determine the effects of the silica and carbon black-supported processing aids on the physical properties and processability of the elastomeric formulations after six months of ambient storage.

The elastomeric stock formulations were prepared according to Table III, below, and the physical properties were evaluated after curing at 170°C for 20 minutes, followed by six months of ambient aging. The data for the physical properties and processability of the elastomeric formulations for the ambient aging study are shown in Table IV, below.

TABLE III	
Basic Formulation of Elastomeric Stock (C-CC)	
Component	Parts
SBR	75
NR	25
Oil	15
carbon black	35
silica	VARIABLE
stearic acid	1.5

TABLE III	
Basic Formulation of Elastomeric Stock (C-CC)	
Component	Parts
wax	1.0
process aid	VARIABLE
antioxidant	0.95
sulfur	1.7
CBS	1.5
DPG	0.5

Table III Continued						
Final Elastomeric Stock Formulations Examples 7-12						
Example	7	8	9	10	11	12
46% SO on Silica ^a	3.3	3.3	---	---	---	---
47% OS on Silica ^b	---	2.5	---	---	---	---
5% SO/3.8% OS on Silica ^c	---	---	32.9	---	---	---
5% SO/3.8% OS on Silica ^d	---	---	---	32.9	---	---
Sorbitan Oleate (SO)	---	---	---	---	1.65	1.65
Octyl triethoxysilane (OS)	1.25	---	---	---	1.25	1.25

WO 00/32684

PCT/US99/27890

Table IV Physical Properties of Elastomeric Formulations After Ambient aging for 6 months						
Example	7	8	9	10	11	12
Mooney Viscosity						
ML 1+4/100°C	77	80.8	78.9	78.9	74.8	78.1
MDR Monsanto Cure at 165°C						
ML	2.97	3.62	3.5	3.69	3.29	3.47
MH	16.12	19.65	19.02	19.62	18.72	16.49
ts2	2:52	2:42	3:04	3:05	2:49	2:54
tc90	14:27	10:47	9:37	9:11	9:41	14:00
tan δ at MH	0.2	0.093	0.102	0.103	0.091	0.189
Ring Tensile at 24°C						
50% Modulus,psi	181	159	172	166	171	165
100% Modulus, psi	333	286	316	296	310	294
200% Modulus, psi	778	676	754	691	740	696
300% Modulus, psi	1415	1242	1389	1273	1375	1288
Tensile Strength, psi	2551	2233	2442	2298	2548	2438
% Elongation	448	445	441	447	454	461
Break energy, in-lbs/in ²	4735	4088	4521	4235	4731	4605
Ring Tensile at 100°C						
50% Modulus,psi	131	131	146	153	146	139
100% Modulus, psi	244	240	267	274	266	250
200% Modulus, psi	541	532	596	596	590	546

Table IV Physical Properties of Elastomeric Formulations After Ambient aging for 6 months						
Example	7	8	9	10	11	12
300% Modulus, psi	973	963	1073	1076	1069	982
Tensile Strength, psi	1285	1400	1356	1433	1430	1396
% Elongation	367	394	356	369	371	388
Break energy, in-lbs/in ²	2024	2353	2069	2266	2270	2330
New Lambourn at 65%, g lost	179	181	157	147	158	149
New Lambourn at 65%, INDEX	0.145	0.148	0.1456	0.1506	0.1454	0.1481
Ring Tear at 171°C, psi	0.97	0.95	0.96	0.93	0.96	0.95
Wet Stanley London(#/std)	53/48.5	57/48.5	53/48.5	53/48.5	56/48.5	53/48.5
Shore A, at RT	66.4	67	67.7	67.5	65.8	64.1
Shore A at 50°C	63.6	64.3	64.8	64.9	63.9	64.1
Rheometrics at 7% Strain						
Tan δ at 24°C	0.1779	0.169	0.181	0.1843	0.159	0.1724
24°C G' x 10 ⁻⁷ at 7%	0.628	0.605	0.657	0.739	0.491	0.577
δ G' x 10 ⁻⁷ at 24°C	4.772	4.224	5.233	5.909	3.13	4.087
24°C G' x 10 ⁻⁷ at 14.5%	2.652	2.779	2.779	3.009	2.48	2.572
tan δ at 50°C	0.15	0.1391	0.1524	0.1544	0.1417	0.1412
50°C G' x 10 ⁻⁷ at 7%	0.462	0.441	0.482	0.521	0.38	0.401
δ G' x 10 ⁻⁷ at 50°C	3.648	3.374	3.941	4.428	2.829	2.995
50°C G' x 10 ⁻⁷ at 14.5%	2.417	2.536	2.477	2.644	2.151	2.281

It is apparent from the data contained in Table IV, that elastomeric formulations containing a silica-supported or carbon black-supported processing aid selected from the group consisting of an alkyl alkoxysilane, fatty acid ester of hydrogenated or non-hydrogenated C₅ and C₆ sugars, e.g., sorbitan, and
5 ethoxylated derivatives of fatty acid esters of these sugars provide physical properties, after six months of ambient aging, comparable to the control elastomeric formulation containing 3 phr of Si69 as a processing aid (C-DD).

Thus, it should be evident that the process of the present invention is useful in improving the processability of formulations of diene polymer
10 elastomers containing silica filler by reducing the viscosity of silica-filled elastomeric vulcanizable compounds. It is further demonstrated that the present invention provides vulcanizable silica-filled elastomeric compounds having enhanced physical properties. Practice of the present invention allows a reduction of Si69 which is added to vulcanizable rubber compositions
15 containing silica fillers. The reduction can be effected by the addition of the processing aids described herein, mineral and non-mineral fillers as well as combinations of more than one.

CLAIMS:

1. A process for the preparation of a silica-filled, vulcanized elastomeric compound comprising:

- (a) mixing
 - (1) 100 parts by weight of an elastomer;
 - (2) from 5 to 100 parts by weight of a reinforcing filler selected from the group consisting of silica filler or mixtures thereof with carbon black, per 100 parts of said elastomer, wherein the silica filler has a BET surface area of 150 to 220m²/g;
 - (3) from 0.1 to 150 percent by weight, based on said silica filler, of a combination of an alkylalkoxysilane and an additional processing aid selected from the group consisting of fatty acid esters of hydrogenated and non-hydrogenated C₅ and C₆ sugars, polyoxyethylene derivatives of fatty acid esters of hydrogenated and non-hydrogenated C₅ and C₆ sugars and mixtures thereof;
 - (4) optionally from 0 to 40 parts by weight of a non-reinforcing filler, per 100 parts elastomer;
 - (5) optionally from 0 to 20 percent by weight of bis[(triethoxysilyl)-propyl]tetrasulfide, based upon the weight of said silica filler; and
 - (6) a cure agent;

wherein said alkylalkoxysilane and said additional processing aid are first mixed with and supported on at least some of either said silica reinforcing filler or said non-reinforcing filler prior to mixing with said elastomer,

and wherein the minimal amount for the alkylalkoxysilane and said additional processing aid is about one part by weight; and

- (b) effecting vulcanization.

2. The process of claim 1, wherein the alkylalkoxysilane is represented by the formula (R₁)₂Si(OR₂)₂ or R₁Si(OR₂)₃, wherein each R₁ independently is selected from the group consisting of C₁ to C₁₈ aliphatic and C₅ to C₁₂ cycloaliphatic; and

wherein the alkoxygroups are the same or are different, each R_2 independently containing from one to 6 carbon atoms.

3. The process of claim 2, wherein the alkylalkoxysilane is selected from the group consisting of octyltriethoxy silane, octyltrimethoxy silane, (3-glycidoxypropyl)trimethoxy silane, (3-glycidoxypropyl)triethoxy silane, hexyltrimethoxy silane, ethyltrimethoxy silane, propyltriethoxy silane, cyclohexyltrimethoxy silane, cyclohexyltriethoxy silane, dimethyldimethoxy silane, 3-chloropropyltriethoxy silane and i-butyltriethoxy silane.

4. The process of any one of claims 1 to 3, wherein the elastomer is a diene monomer homopolymer or a copolymer of at least one diene and at least one monomer selected from the group consisting of monovinyl aromatic monomers and triene monomers.

5. The process of any one of claims 1 to 4, wherein the process further includes mixing insoluble sulfur prior to vulcanizing.

6. The process of any one of claims 1 to 5, wherein the elastomer is styrene-butadiene rubber.

7. The process of any one of claims 1 to 6, wherein the elastomer is a copolymer of styrene-butadiene rubber and butyl rubber.

8. The process of any one of claims 1 to 7, wherein the elastomer further contains natural rubber.

9. The process of any one of claims 1 to 8, wherein the fatty acid esters of hydrogenated and non-hydrogenated C_5 and C_6 sugars are selected from the group consisting of sorbitan monooleate, sorbitan diolate, sorbitan trioleate, sorbitan sesquioleate, sorbitan laurate, sorbitan palmitate and sorbitan stearate, and wherein

the polyoxyethylene derivatives of fatty acid esters of hydrogenated and non-hydrogenated C5 and C6 sugars are selected from the group consisting of POE (20) sorbitan stearate; POE (20) sorbitan oleate; POE (20) sorbitan trioleate; POE (20) sorbitan sesquioleate; POE (20) sorbitan laurate and POE (20) sorbitan palmitate.

10. The process of any one of claims 1 to 9, wherein the additional processing aid is a mixture of at least one fatty acid ester of hydrogenated and non-hydrogenated C₅ and C₆ sugars and at least one polyoxyethylene derivative of a fatty acid ester of hydrogenated and non-hydrogenated C₅ and C₆ sugars.

11. The process of any one of claims 1 to 10, wherein the amount of said carbon black reinforcing filler ranges from 0 to 50 parts by weight, per 100 parts by weight of elastomer, and the amount of said reinforcing silic filler ranges from 1 to 100 parts, per 100 parts of elastomer, with the proviso that where carbon black is 0, at least 30 phr of silica is employed.

12. A compound obtained from a process of any one of claims 1 to 11.

13. A pneumatic tire comprising tread stock vulcanized from a compound of claim 12.

14. A pneumatic tire comprising tread stock obtained from a process of any one of claims 1 to 11.