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(54) **COMPOSITION DE CAOUTCHOUC CONTENANT DE LA
SILICE**

(54) **SILICA-CONTAINING RUBBER COMPOSITION**

(57) Cette invention concerne une composition élastomère comprenant : 1) un mélange mère contenant une solution vinylique SBR et de la silice, qui renferme, de préférence, de 40 à 120 parties, en poids, de silice par 100 parties, en poids, de polymère; et 2) un mélange mère contenant un polybutadiène à haute teneur en motif cis et de la silice, qui renferme, de préférence, de 40 à 120 parties, en poids, de silice par 100 parties, en poids, de polymère, et dans lequel la silice a été rendue hydrophobe.

(57) The invention provides an elastomeric composition which comprises 1) a vinyl solution SBR/silica-containing masterbatch, which contains preferably from 40 to 120 parts by weight of silica per 100 parts by weight of polymer, and 2) a high cis polybutadiene/silica-containing masterbatch, which contains preferably from 40 to 120 parts by weight of silica per 100 parts by weight of polymer wherein silica has been hydrophobicized.

ABSTRACT

The invention provides an elastomeric composition which comprises 1) a vinyl solution SBR/silica-containing masterbatch, which contains preferably from 40 to 120 parts by weight of silica per 100 parts by weight of polymer, and 2) a high cis polybutadiene/silica-containing masterbatch, which contains preferably from 40 to 120 parts by weight of silica per 100 parts by weight of polymer wherein silica has been hydrophobicized.

The present invention relates to elastomeric compositions containing hydrophobicized silica. Elastomeric compositions of the invention are suitable, for example, for the manufacture of tires, tire tread hose, hose, industrial drive belts, and shoe soles.

BACKGROUND OF THE INVENTION

In recent years, there has developed a considerable interest in silica reinforced tires, particularly since the appearance in 1992 of the *Groupe Michelin* (G-M) patents (EP 05 10 01 227 A 1; AU-A-111 77 192) indicating that tires made with tread formulations incorporating silica enjoy some important performance advantages over those based on conventional carbon black filler. Improvements are claimed for this "Green Tire" in the areas of (a) lower rolling resistance, (b) better traction on snow and (c) lower noise generation, when compared with conventional tires filled with carbon black.

Rubber for tires is often supplied by a rubber supplier to a tire manufacturer in the form of a masterbatch containing an elastomer, which is typically a hydrocarbon rubber, an oil extender and a filler. The traditional filler 20 has been carbon black in the form of fine particles. These particles have hydrophobic surface characteristics and will therefore disperse easily within the hydrophobic elastomer. In contrast, silica has a very hydrophilic surface, and considerable difficulty has been encountered in dispersing silica in the hydrophobic rubber elastomer.

In the past, efforts have been made to make masterbatches from elastomer dispersions and aqueous

dispersions of silica pigment, such as those referred to and attempted by Burke, in U.S. Patent No. 3,700,690. Burke attempted to overcome the previously known difficulties of incorporating fine particles of silica uniformly into a masterbatch. At the time of the Burke invention, there was no known elastomer-silica masterbatch offered in the commercial market. Similarly today, to applicant's knowledge, there are no commercially available elastomer-silica masterbatches in the market, despite the efforts of Burke.

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SUMMARY OF THE INVENTION

The present invention is thus directed to elastomeric compositions which comprise

1) a vinyl solution SBR/silica-containing masterbatch, which contains preferably from about 40 to about 120 parts by weight of silica per 100 parts by weight of polymer, and

2) a high cis polybutadiene/silica-containing masterbatch, which contains preferably from about 40 to about 120 parts by weight of silica per 100 parts by weight of polymer;

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wherein silica has been hydrophobicized.

Preferably the vinyl solution SBR portion of component 1) is present in from about 40 to about 90 parts by weight and the polybutadiene portion of component 2) is present in from about 60 to about 10 parts by weight.

By this invention we have achieved improved traction, abrasion and rolling resistance characteristics in compositions of elastomer blends containing hydrophobicized silica.

DESCRIPTION OF PREFERRED EMBODIMENTS

The vinyl solution SBR is suitably prepared in solution and has a styrene content between about 15 and 25% by weight and a glass transition temperature (T_g) of between 0°C and -80°C. when measured by differential scanning calorimeter. The content of vinyl bonds in the butadiene fraction incorporated can be between about 33 and about 73%, the content of trans-1,4 bonds can be between 20 and 80%, and the content of cis 1,4 bonds is complementary to the contents of vinyl bonds plus trans-1,4 bonds. The vinyl bonds content of the copolymer is preferably greater than 50%. Particularly preferred is Buna VSL 5025-1 (formerly Buna VSL 1950S25, supplied by Bayer) which is a co-polymer of styrene and butadiene, the styrene content being about 25% and the vinyl content in the butadiene portion being about 67%.

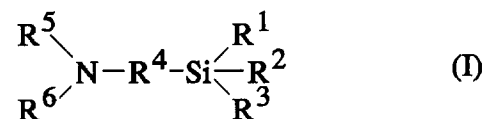
The high cis polybutadiene is preferably polybutadiene having more than 90% cis-1,4 bonds obtained by known methods of catalysis with the use of transition metals as described, for instance in French Patent No. 143 6607. Particularly, preferred is Taktene 1203 (available from Bayer), which has a cis content of about 96%.

The composition preferably contains from about 30 to about 100 parts per 100 parts of total polymer (phr) of silica. Preferably it also contains from about 25 to about 50 parts per 100 parts of total polymer (phr) of aromatic oil, selected from those known in rubber processing.

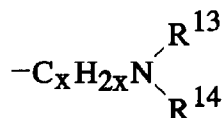
A preferred method for hydrophobicizing silica particles is that of our copending Canadian Application Serial

No. 2,205,789, and comprises the following steps:

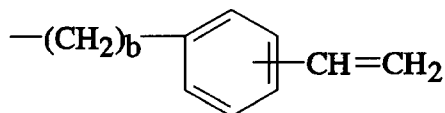
a) treating the silica particles with a compound of formula I



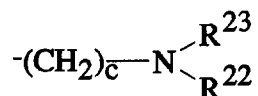
or an acid addition or quaternary ammonium salt thereof, in which at least one of R^1 , R^2 and R^3 , preferably two of R^1 , R^2 and R^3 and most preferably R^1 , R^2 and R^3 are hydroxyl or hydrolysable groups, R^4 is a divalent group that is resistant to hydrolysis at the $\text{Si}-\text{R}^4$ bond, R^5 is hydrogen, a C_{1-30} alkyl or C_{2-30} mono-, di- or triunsaturated alkenyl group, or R^5 is a group of formula



in which x is an integer from 2 to 10, R^{13} and R^{14} are each hydrogen, C_{1-18} alkyl, C_{2-18} mono-, di- or triunsaturated alkenyl, phenyl, a group of formula

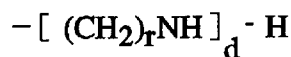


wherein b is an integer from 1 to 10, or a group of formula

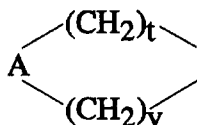


wherein c is an integer from 1 to 10 and R^{22} and R^{23} which may be the same or different, are each hydrogen, C_{1-10} alkyl or C_{2-10} alkenyl, provided that there is no double bond in the position alpha to the nitrogen atom, or a group of formula

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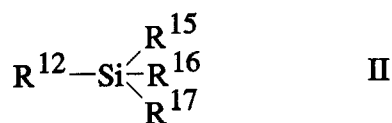


wherein r is an integer from 1 to 6 and d is an integer from 1 to 4, R^6 may be any of the groups defined for R^5 , or R^5 and R^6 may together form a divalent group of formula



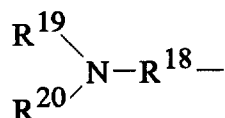
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in which A is a -CHR or -NR group in which R is hydrogen or a C_{1-30} alkyl or C_{2-30} alkenyl group, or A is an oxygen or sulfur atom and t and v are each independently 1, 2, 3 or 4; provided that the sum of t and v does not exceed 6, and is preferably 4; and (b) thereafter adding to the treated particles a compound of the formula II



in which R^{15} , R^{16} and R^{17} have the same definitions as R^1 , R^2 and R^3 , and R^{12} is a C_{8-30} alkyl group or a C_{8-30} mono-, di- or triunsaturated alkenyl group, either of which can be interrupted by one or more aryl groups, preferably phenyl groups, or a group of formula

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or an acid addition or quaternary ammonium salt thereof in which R^{18} is a divalent group resistant to hydrolysis at the $\text{Si}-\text{R}^{18}$ bond, R^{19} is hydrogen, a C_{1-30} alkyl group, a C_{2-30} mono-, di- or triunsaturated alkenyl group, a substituted aromatic group, for example the phenylene group $-(\text{C}_6\text{H}_4)-$, the biphenylene group $-(\text{C}_6\text{H}_4)-(\text{C}_6\text{H}_4)-$, the $-(\text{C}_6\text{H}_4)-\text{O}-(\text{C}_6\text{H}_4)-$ group or the naphthylene group, $-(\text{C}_{10}\text{H}_6)-$, that is substituted by a C_{1-20} alkyl or C_{2-20} mono-, di- or triunsaturated alkenyl group, and R^{20} may be any of the groups defined for R^{19} , with the provisos that R^{19} and R^{20} do not have a tertiary carbon atom adjacent to the nitrogen atom and that at least one of R^{19} and R^{20} has a carbon chain at least 8 carbon atoms in length uninterrupted by any heteroatoms.

Preferably the hydrophobizing process is carried out in an aqueous solution, dispersion or slurry, so that the

product of the process is an aqueous dispersion or slurry of hydrophobicized silica particles. In one preferred embodiment the slurry or dispersion is then mixed with a hydrocarbon solution of the vinyl solution SBR or of the high cis polybutadiene and then dried to form a silica-filled masterbatch. Owing to the hydrophobicized nature of the silica filler, it is well dispersed.

10 In a preferred embodiment the hydrophobicizing treatment is carried out in an aqueous dispersion or slurry and the concentration of the aqueous dispersion or slurry of silica particles may be between 1 and 30 percent by weight of silica in water, preferably between 5 and 25 percent by weight of silica and most preferably between 8 and 22 percent by weight of silica. Dried amorphous silica suitable for use in accordance with the invention may have a mean agglomerate particle size between 5 and 100 microns, preferably between 10 and 50 microns and most preferably between 10 and 25 microns. It is preferred that less than 10 percent by volume of the agglomerate particles are below 5 microns or over 50 microns
20 in size. A suitable amorphous dried silica moreover has a BET surface area, measured in accordance with DIN (Deutsche Industrie Norm) 66131, of between 50 and 450 square meters per gram and a DBP absorption, as measured in accordance with DIN 53601, of between 150 and 400 grams per 100 grams of silica, and a drying loss, as measured according to DIN ISO 787/II, of from 0 to 10 percent by weight. If filter cake is used then it may be made by any known means such as described in Ullmann's Encyclopedia of Industrial Chemical Vol A23 pages

642-643, VCH Publishers, ©1993; the filter cake has a preferred solids content of between 5 and 30 percent by weight and most preferably between 15 and 25 percent by weight and it is redispersed in water in accordance with the invention to give a silica concentration of between 5 and 20 percent by weight and most preferably between 8 and 12 percent by weight. It is preferred to use a filter cake.

10 If a never-filtered slurry prepared from the known reaction of a solution of alkali metal silicate with either mineral acid or carbon dioxide is used, then it is needed only that the solids content of the never-filtered slurry be between 5 and 10 percent by weight of silica. The slurry temperature may be between 0 and 100 degrees Celsius if the process is conducted at atmospheric pressure or between 0 and 135 degrees Celsius if the operation is conducted in a pressure vessel. Most preferably the process is conducted at atmospheric pressure in which case the preferred temperature is between 30 and 95 degrees Celsius and most preferably between 45 and 90 degrees Celsius.

20 It is desirable that, prior to the addition to the silica particles of the compound of formula I, the dispersion or slurry shall have a pH in the range from about 6.8 to about 7.2. If necessary, the pH can be adjusted by addition of acid or alkali, for example mineral acid or alkali metal hydroxide, such as sodium hydroxide. These can be added as such or in aqueous solution.

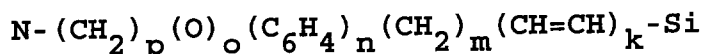
In the compound of formula I it is preferred that all three of the groups R^1 , R^2 and R^3 are hydrolysable.

Suitable groups R^1 include hydroxyl groups and hydrolysable groups of formula OC_pH_{2p+1} , where p has a value from 1 to 10. The alkyl chain can be interrupted by oxygen atoms, to give groups, for example, of formula CH_3OCH_2O- , $CH_3OCH_2OCH_2O-$, $CH_3(OCH_2)_4O-$, $CH_3OCH_2CH_2O-$, $C_2H_5OCH_2O-$, $C_2H_5OCH_2OCH_2O-$, or $C_2H_5OCH_2CH_2O-$. Other suitable hydrolysable groups include phenoxy, acetoxy, chloro, bromo, iodo, ONa, OLi, OK or amino or mono- or dialkylamino, wherein the alkyl group(s) have 1 to 30 carbon atoms.

R^2 and R^3 can take the same values as R^1 , provided that only one of R^1 , R^2 and R^3 is chloro, bromo or iodo. Preferably only one or two of R^1 , R^2 and R^3 is hydroxyl or ONa, OLi or OK.

Groups R^2 and R^3 that are not hydrolysable include C_{1-10} alkyl, C_{2-10} mono- or diunsaturated alkenyl, and phenyl. R^2 and R^3 can also each be a group $-R^4-NR^5R^6$, discussed further below. It is preferred that R^1 , R^2 and R^3 are all the same and are CH_3O- , C_2H_5O- or C_3H_8O- . Most preferably they are all CH_3O- .

The divalent group R^4 is preferably such that $N-R^4-Si$ is of the formula



in which k, m, n, o and p are all whole numbers. The value of k is 0 or 1, the value of m is from 0 to 20 inclusive, the value of n is 0, 1 or 2, the value of o is 0 or 1 and the value of p is from 0 to 20 inclusive, with the provisos that the sum of the values of k, m, n, o and p is at least 1 and

not more than 20 and that if o is 1, then p is 1 or greater and the sum of k, m and n is 1 or greater, i.e. that the Si atom is linked directly to a carbon atom. There should be no hydrolysable bond between the silicon and nitrogen atoms. Preferably m is 3 and 1, n, o and p are all 0, i.e., R⁴ is -CH₂CH₂CH₂-.

The group R⁵ is preferably a C₈₋₂₀ monounsaturated alkenyl group, most preferably a C₁₆₋₁₈ monounsaturated alkenyl group. R⁶ is preferably hydrogen.

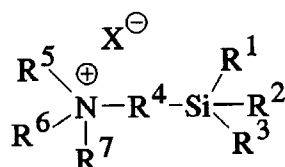
10 Suitable compounds of formula I include, but are not limited to: 3-aminopropylmethyldiethoxysilane, N-2-(vinylbenzylamino)-ethyl-3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, trimethoxysilylpropyldiethylenetriamine, N-2-(aminoethyl)-3-aminopropyltris(2-ethylhexoxy)silane, 3-aminopropyldiisopropylethoxysilane, N-(6-aminoethyl)aminopropyltrimethoxysilane, 4-aminobutyltriethoxysilane, 4-aminobutyldimethylmethoxysilane, triethoxysilylpropyldiethylenetriamine, 3-aminopropyltris(methoxyethoxyethoxy)silane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, 20 N-2-(aminoethyl)-3-aminopropyltris(2-ethylhexoxy)silane, 3-aminopropyldiisopropylethoxysilane, N-(6-aminoethyl)aminopropyltrimethoxysilane, 4-aminobutyltriethoxysilane, and (cyclohexylaminomethyl)methyldiethoxysilane.

Preferred compounds of formula (I) include those in which R⁵ is hydrogen and R⁶ is the alkenyl group from the following: soya alkyl, tall oil alkyl, stearyl, tallow alkyl, dihydrogenated tallow alkyl, cocoalkyl, rosin alkyl, and palmityl, it being understood that in this case the alkyl may

include unsaturation.

It is preferred that at least one of R⁴, R¹³ and R¹⁴ has a chain of at least 8 carbon atoms, more preferably at least 10 carbon atoms, uninterrupted by any heteroatom.

The compound of formula I can be used as the free base, or in the form of its acid addition or quaternary ammonium salt, i.e.



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wherein R¹, R², R³, R⁴, R⁵ and R⁶ are as defined above and R⁷ is hydrogen, a C₁₋₃₀ alkyl group or C₂₋₃₀ mono-, di- or triunsaturated alkenyl group, and X is an anion. X is suitably chlorine, bromine, or sulphate, of which chlorine and bromine are preferred, and R⁷ is preferably hydrogen.

Non-limiting examples of suitable salts of compounds of formula I include N-oleyl-N-[(3-triethoxysilyl)propyl] ammonium chloride, N-3-aminopropylmethyldiethoxysilane hydrobromide, (aminoethylaminomethyl)phenyltrimethoxysilane hydrochloride, N-[(3-trimethoxysilyl)propyl]-N-methyl, N-N-diallylammonium chloride, N-tetradecyl-N,N-dimethyl-N-[(3-trimethoxysilyl)propyl] ammonium bromide, 3[2-N-benzylaminoethylaminopropyl]trimethoxysilane hydrochloride, N-octadecyl-N,N-dimethyl-N-[(3-trimethoxysilyl)propyl] ammonium bromide, N-[(trimethoxysilyl)propyl]-N-tri(n-butyl) ammonium chloride, N-octadecyl-N-[3-triethoxysilyl]propyl] ammonium chloride, and

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N-2-(vinylbenzylamino)ethyl-3-aminopropyl-trimethoxysilane hydrochloride.

It is preferred to use the compound of formula I in salt form. The most preferred compound is N-oleyl-N-[(3-trimethoxysilyl)propyl] ammonium chloride.

The amount of the compound of formula I may be between 0.1 and 20 percent by weight of the silica particles in the slurry (dry basis) and preferably between 0.25 and 10 percent by weight and most preferably between 0.5 and 2 percent by weight. The amount of compound of formula I required varies inversely with the particle size. The compound may be added to the slurry in its natural state, either as a liquid or a solid. However, to facilitate dispersion, it is preferred where possible to add the compound as a liquid. If the melting point of the compound is below 95 degrees Celsius then it is preferred to add it to the slurry in a molten state at a temperature at least 5 degrees above the melting point, provided the temperature of the compound in the liquified state does not exceed 100 degrees Celsius and provided that the compound does not decompose under these conditions. If the melting point exceeds 95 degrees Celsius then it is most preferred to use a solvent. Preferred solvents are alcohols containing 1 to 5 carbon atoms and most preferably those containing 1 to 3 carbon atoms, that is to say methanol, ethanol, n-propanol or isopropanol. If the compound of formula I is an alkoxy silane, then most preferably the alkoxy group of the solvent alcohol will be the same as the alkoxy group of the alkoxy silane. For example, if the

compound of formula I is a methoxysilane, then the preferred solvent is methanol. The concentration of the compound in the solvent may be from 10 to 90 percent by weight and most preferably between 25 and 75 percent by weight and most preferably 50% by weight. The solution is prepared and added to the slurry at a temperature between a lower limit of 0 degrees Celsius and an upper limit which is at least 10 degrees below the boiling point of the solvent or 95 degrees Celsius, or the temperature of the slurry, whichever is lower.

10 The dispersion of the compound is effected by mixing.

It is preferred that, after the compound of formula I has been added, the equivalent balance (EB) should be calculated. The EB is used to determine whether mineral acid or alkali metal hydroxide, or solution thereof, should be added. The equivalent balance (EB) may be determined from the absolute value of the sum of the group values of X, R^1 , R^2 and R^3 and the magnitude of the sum of the group contributions of X, R^1 , R^2 and R^3 together with the weight added and the molecular weight of the compound of formula I, according to

20 the following scheme: The group contribution of X for either X=Cl or X=Br is -1, thus if X is present it is given a value of -1. The group contribution of each of R^1 , R^2 and R^3 is generally zero for all groups except as follows: if the group is CH_3COO , Cl or Br, in which case it is -1, or if it is amine, ONa, OK or OLi in which case it is +1. If the sum of the group contributions for X, R^1 , R^2 and R^3 is zero, then no adjustment with mineral acid or alkali metal hydroxide (or solutions thereof) is necessary. If the sum of the group

values is a positive integer, then adjustment with mineral acid is necessary, and if it is negative, then adjustment with alkali metal hydroxide is indicated.

For example, where $R^1 = \text{OCH}_3$, $R^2 = \text{CH}_3$, $R^3 = \text{Cl}$ and $X = \text{Br}$, the sum of the group values (g.v.) is:

$$\Sigma = (\text{g.v. OCH}_3) + (\text{g.v. CH}_3) + (\text{g.v. Cl}) + (\text{g.v. Br}) = (0) + (0) + (-1) + (-1) = -2$$

The negative sign in front of the sum indicates adjustment with alkali metal hydroxide is required. The number of equivalents of alkali required is given by the equivalent balance (EB) which includes the absolute value of the sum of the group contributions ($|\Sigma|$) as a scaling factor:

$$\text{EB} = \frac{|\Sigma| \times \text{weight in grams of the chemical added}}{\text{molecular weight of the added chemical}}$$

In continuing the example, if a process were scaled so as to require 6,000 grams of a chemical with a molecular weight of 350 grams and the sum of the group values gave -2, then EB would be calculated as follows:

$$\text{EB} = -2 \times 6000/350 = -34.28 \text{ gram-equivalents}$$

It would be required in this example to add 34.28 gram-equivalents of alkali metal hydroxide. Sodium hydroxide is the preferred alkali metal hydroxide. The weight of sodium hydroxide required would be:

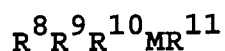
$$\text{Weight} = (\text{EB}) \times (\text{Equivalent Weight of NaOH}) = 34.28 \times 40.0 = 1371.2 \text{ grams}$$

The preferred technique is to dissolve the alkali metal hydroxide or mineral acid in water so as to obtain a concentration between 5 and 25% by weight and most preferably

between 5 and 10% by weight prior to adding the solution to the slurry.

It is known to incorporate a coupling agent into rubber that is intended to be vulcanized and used, for instance, in tires. Suitable coupling agents include those described in United States Patent No. 4,704,414, EP 0 670 347 A1 and German Published Patent Specification No. 44 35 311 A1, the disclosures of which are incorporated by reference. One suitable coupling agent is bis[3-(triethoxysilyl)propyl]tetrasulfane, available under the trade mark Si-
 10 69, and another is bis[2-(triethoxysilyl)ethyl]tetrasulfane, available under the trade mark Silquest RC-2. In the past, achieving a good balance between the coupling agent and silica particles without scorching or premature curing has proven difficult. In accordance with Application No. 2,205,789, if silica particles, are being treated to render them hydrophobic for use in rubber which is subsequently to be vulcanized, it is possible to include a step of adding a coupling agent in
 20 the process so that the coupling agent becomes attached to the surface of the hydrophobicized silica particles and becomes dispersed in the rubber with the silica particles.

Thus, a coupling agent may be added to the dispersion after the addition of the compound of formula I but before the compound of formula II is added. The coupling agent is added after any addition of mineral acid or alkali metal hydroxide that is indicated by the calculation of the EB. Suitable coupling agents include compounds of formula



in which at least one of R^8 , R^9 and R^{10} , preferably two of R^8 , R^9 and R^{10} and most preferably R^8 , R^9 and R^{10} , are hydroxyl or hydrolysable groups. The groups R^8 , R^9 and R^{10} are bound to the atom M, which is silicon, titanium or zirconium. The group R^8 may be hydroxyl or OC_pH_{2p+1} where p is from 1 to 10 and the carbon chain may be interrupted by oxygen atoms, to give groups, for example, of formula CH_3OCH_2O- , $CH_3OCH_2OCH_2O-$, $CH_3(OCH_2)_4O-$, $CH_3OCH_2CH_2O-$, $C_2H_5OCH_2O-$, $C_2H_5OCH_2OCH_2O-$ or $C_2H_5OCH_2CH_2O-$. Alternatively R^8 may be phenoxy. If M is titanium or zirconium then R^8 may be the neopentyl(diallyl)oxy group, but not if M is silicon. The group R^9 may be the same as R^8 . If M is silicon then R^9 may also be a C_{1-10} alkyl group, a phenyl group, or a C_{2-10} mono- or diunsaturated alkenyl group. If M is titanium or zirconium then R^9 may be the neopentyl(diallyl)oxy group, but not if M is silicon. Further, R^9 may be the same as the group R^{11} described below.

R^{10} may be the same as R^8 , but it is preferred that R^8 , R^9 and R^{10} are not all hydroxyl. If M is silicon then R^{10} may also be C_{1-10} alkyl, phenyl, C_{2-10} mono- or diunsaturated alkenyl. If M is titanium or zirconium then R^{10} may be the neopentyl(diallyl)oxy group, but not if M is silicon. Further R^{10} may be the same as the group R^{11} described below.

The group R^{11} attached to M is such that it may participate in a crosslinking reaction with unsaturated polymers by contributing to the formation of crosslinks or by otherwise participating in crosslinking. In the case where M is silicon, then R^{11} may have the one of the following

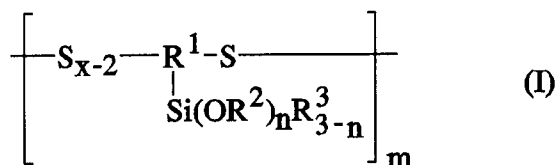
structures: R^{11} may represent the allyl group $-H_2CCH=CH_2$, the vinyl group $-CH=CH_2$, the 5-bicycloheptenyl group or the group described by $-(alk)_e(Ar)_fSi_i(alk)_g(Ar)_hSiR^8R^9R^{10}$ where R^8 , R^9 and R^{10} are the same as previously defined, alk is a divalent straight hydrocarbon group having between 1 and 6 carbon atoms or a branched hydrocarbon group having between 2 and 6 carbon atoms, Ar is either a phenylene $-C_6H_4-$, biphenylene $-C_6H_4-C_6H_4-$ or $-C_6H_4-OC_6H_4-$ group and e, f, g and h are either 0, 1 or 2 and i is an integer from 2 to 8 inclusive with the provisos that the sum of e and f is always 1 or greater than 1 and that the sum of g and h is also always 1 or greater than 1. Alternately, R^{11} may be represented by the structures $(alk)_e(Ar)_fSH$ or $(alk)_e(Ar)_fSCN$ where e and f are as defined previously. It is moreover permissible that R^{11} has the structure $-(CH=CH)_k(CH_2)_m(C_6H_4)_n(O)_o(CH_2)_pR^{13}$ wherein k, m, n and o and p are all whole numbers and R^{13} represents the acryloxy $CH_2=CHCOO-$ or the methacryloxy $CH_2=CCH_3COO-$ group. Further, the value of k may be between 0 or 1, m may be from 0 to 20 inclusive, n may be between 0 and 2, o may be 0 or 1, and p may be from 0 to 20 inclusive, with the provisos that the sum of k, m, n and o is at least 1 and not greater than 20, and that if n is 1 or 2 or o is 1, then p is 1 or greater. It is most preferable that $m=3$ and k, n, o and p are all 0.

Preferably R^8 , R^9 and R^{10} are all either OCH_3 , OC_2H_5 or OC_3H_8 groups and most preferably all are OCH_3 groups and it is most preferred that the coupling agent is bis[(3-triethoxysilyl)propyl]-tetrasulfane (Si-69). The amount of

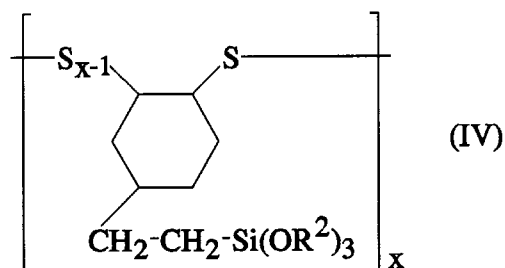
coupling agent to add is optional; levels between 2 and 10 percent by weight of the silica in the slurry (dry basis) are preferred. The dispersion of the chemical is effected by mixing.

Non-limiting illustrative examples of other coupling agents include the following: bis[(3-trimethoxysilyl)propyl]tetrasulfane (Si-168), bis[2-(triethoxysilyl)ethyl]tetrasulfane (Silquest RC-2), bis[2-(trimethoxysilyl)ethyl]tetrasulfane, bis[2-(triethoxysilyl)ethyl]trisulfane, 10 bis[3-(trimethoxysilyl)propyl]disulfane, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropylmethyldiethoxysilane, 3-mercaptoethylpropylethoxymethoxysilane, 1,3-bis(3-acryloxypropyl)tetramethoxydisiloxane, acryloxypropylmethyldimethoxysilane, 3-methacryloxypropyltrimethoxysilane, allyltrimethoxysilane, diallyldiethoxysilane, 5-(bicycloheptenyl)triethoxysilane, 5-(bicycloheptenyl)methylmethoxyethoxysilane, isopropoxytriacyltitanate, diisopropyldimethacryltitanate, diethoxydi(3-mercaptopropoxy)zirconate, triisopropoxy-(2-mercaptoethoxy)zirconate, and 20 di[neopentyl(diallyl)oxy]-di(3-mercaptopropoxy)zirconate.

Other preferred coupling agents include those disclosed in German Published Patent Application 44 35 311 A1. On pages 2 and 3 this discloses oligomers and polymers of sulphur containing organoorganooxysilanes of the general formula



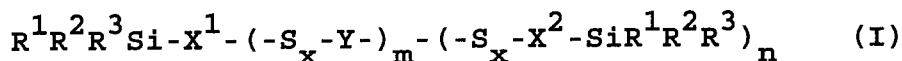
10 in which R^1 is a saturated or unsaturated, branched or unbranched, substituted or unsubstituted hydrocarbon group that is at least trivalent and has from 2 to 20 carbon atoms, provided that there are at least two carbon-sulphur bonds, R^2 and R^3 , independently of each other, are saturated or unsaturated, branched or unbranched, substituted or unsubstituted hydrocarbon groups with 1 to 20 carbon atoms, halogen, hydroxy or hydrogen, n is 1 to 3, m is 1 to 1000, p is 1 to 5, q is 1 to 3 and x is 1 to 8. Preferred compounds are of the general formula



20

wherein R^2 , m and x have the meanings given above, and R^2 is preferably methyl or ethyl. These compounds disclosed in German Patent Application No. 44 35 311 A1 are preferred coupling agents.

Further preferred coupling agents are disclosed in the abovementioned European Patent Application No. 0 670 347 A1, which discloses coupling agents of the general formula

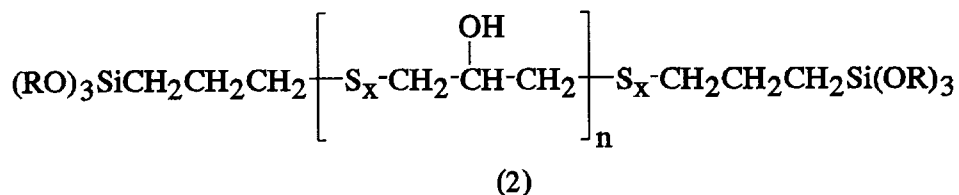


in which R^1 , R^2 and R^3 are the same or different and are C_{1-8} alkyl, C_{1-8} alkoxy, phenyl or phenoxy, provided that at least one of R^1 , R^2 and R^3 is an alkoxy or phenoxy group. X^1 and X^2 are the same or different and are divalent linear or branched, optionally unsaturated C_{1-12} alkyl groups, Y is a di- tri- or tetravalent linear, branched or cyclic C_{1-18} alkyl group that is optionally unsaturated and is optionally substituted by C_{6-12} aryl, C_{1-8} alkoxy or hydroxy groups and which can be interrupted by oxygen, sulphur or nitrogen atoms or aromatic C_{6-12} aryl groups, or Y is a C_{6-12} aryl or heteroaryl group, m is an integer from 1 to 20, n is an integer from 1 to 6 and x is an integer from 1 to 6.

Particularly preferred coupling agents are those of the following general formulae:



in which $R=CH_3$, C_2H_5 , $x=1-6$ and $n=1-10$;

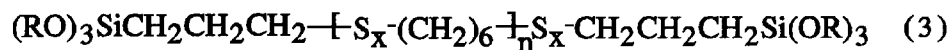


in which

$R = CH_3$, C_2H_5 ,

$$x = 1-6,$$

$$n = 1-10,$$



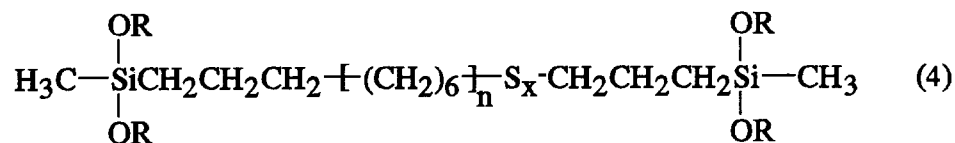
in which

$$R = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7,$$

$$n = 1-10$$

$$x = 1-6,$$

10



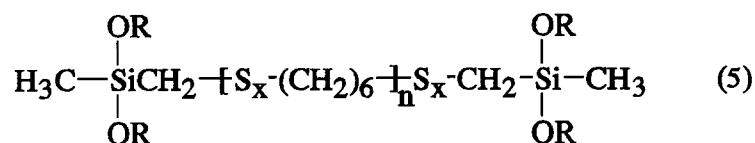
in which

$$R = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7,$$

$$n = 1-10,$$

$$x = 1-6,$$

20



in which

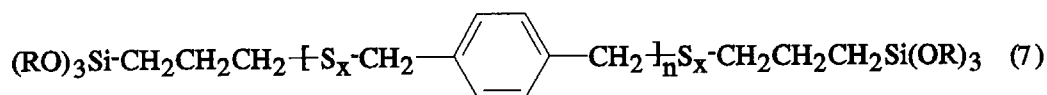
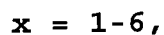
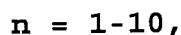
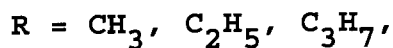
$$R = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7,$$

$$n = 1-10,$$

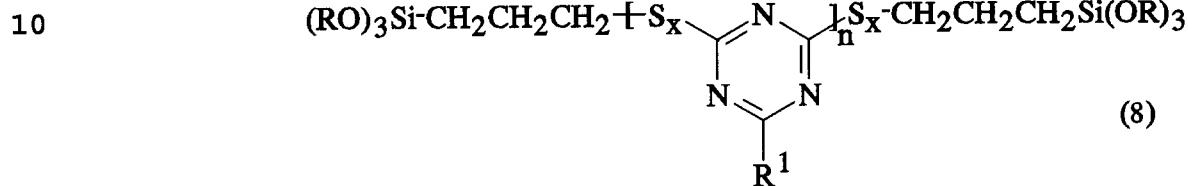
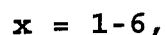
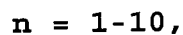
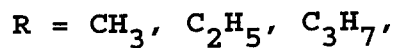
$$x = 1-6,$$



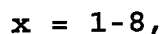
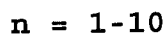
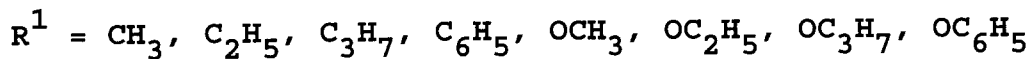
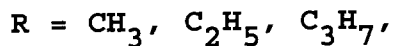
in which



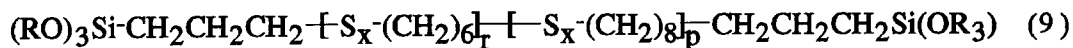
in which



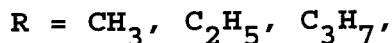
in which



20 and



in which



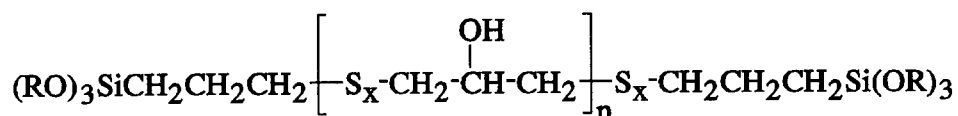
$$r+p = 2-10,$$

$$x = 1-6.$$

Especially preferred are coupling agents of the formulae



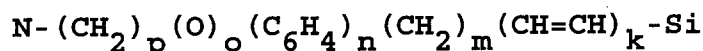
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in which x is 1 to 6 and n is 1 to 4.

20

In step (b), the compound of formula II is added to the treated silica particles. Again, it is preferred that the silica particles are in aqueous slurry or dispersion, and the compound of formula II is added to the slurry or dispersion under intense mixing. In the compound of formula II the possible and preferred values for R^{15} , R^{16} and R^{17} are the same as the possible and preferred values for R^1 , R^2 and R^3 that are discussed above in relation to formula I. If R^{12} is an amino group of formula $-\text{R}^{18}-\text{NR}^{19}\text{R}^{20}$ then preferred values for R^{18} are such that $\text{N}-\text{R}^{18}-\text{Si}$ includes groups of the formula



in which k is 0 or 1, m is 0 to 20 inclusive, n is 0, 1 or 2,

o is 0 or 1 and p is 0 to 20 inclusive, provided that the sum of k, m, n, o and p is at least 1 and not greater than 20, and further provided that if o is 1 then p is also 1 or greater, and the sum of k, m and n is 1 or greater. There should be no hydrolysable group between the silicon and nitrogen atoms. Preferably k, n, o and p are all 0 and m is 3, i.e. R^{18} is $-\text{CH}_2\text{CH}_2\text{CH}_2-$.

R^{12} may be a moiety containing at least one primary, secondary, or tertiary amine nitrogen. In this case the amino group bonded to R^{18} is given by the formula $-\text{NR}^{19}\text{R}^{20}$. R^{19} may be a H or a C_{1-30} alkyl group or a C_{2-30} mono-, di- or triunsaturated alkenyl group. R^{19} may also be a C_{1-20} alkyl-substituted or C_{2-20} alkenyl-substituted aromatic group. The aromatic group may be, for example, the phenylene group $-(\text{C}_6\text{H}_4)-$, the biphenylene group $-(\text{C}_6\text{H}_4)-(\text{C}_6\text{H}_4)-$, the $-(\text{C}_6\text{H}_4)-\text{O}-(\text{C}_6\text{H}_4)-$ group, or the naphthylene group $-(\text{C}_{10}\text{H}_6)-$. R^{20} may be one of the same groups as R^{19} with the further proviso that at least one of R^{19} and R^{20} must contain a continuous carbon chain of at least 8 carbons in length, uninterrupted by any heteroatoms.

As stated above, if R^{19} and R^{20} are other than hydrogen the carbon atom attached to the nitrogen atom is not tertiary. Preferably the carbon atom attached to the nitrogen atom is primary, i.e., $-\text{CH}_2-$.

It is preferred that R^{19} is a mono-unsaturated alkenyl group of 12-20 carbons in length and most preferable that R^{19} is a monounsaturated alkenyl group of 16 to 18 carbons in length. It is most preferable also that R^{20} is H.

Alternatively, R^{12} may be a moiety which contains a mineral acid salt or a quaternary ammonium salt of an amine. The formula of R^{12} may thus be described by the extended formula $-R^{18}-NR^{19}R^{20}.R^{21}_x$ wherein $-R^{18}-$, R^{19} and R^{20} are as previously defined and R^{21} may be a H, or a C_{1-30} alkyl or C_{2-30} mono-, di- or triunsaturated alkenyl group and X is an anion, preferably Cl or Br, although sulphate can be used.

10 There is the further proviso that at least one of R^{19} and R^{20} must contain a continuous carbon chain of at least 8 carbons in length, uninterrupted by any heteroatom. It is preferred to use an amine salt where R^{19} is a mono- or di-unsaturated alkenyl group of 12-20 carbons in length and most preferably that R^{19} is a mono- or di-unsaturated alkenyl group of 16 to 18 carbons in length. It is most preferable also that R^{20} is H and that R^{21} is H and X is chlorine.

20 The amount of the hydrophobic compound of formula II to add is generally between 0.5 and 20 percent by weight of the weight of the silica in the slurry (dry basis), and is inversely proportional to the particle size of the silica particles. The compound may be added to the slurry in its natural state, either as a liquid or a solid. However, to facilitate dispersion, it is preferred where possible to add the compound as a liquid. If the melting point of the compound is below 95 degrees Celsius then it is preferred to add it to the slurry in a molten state at a temperature at least 5 degrees above the melting point, provided the temperature of the compound in the liquified state does not

exceed 100 degrees Celsius and provided that the compound does not decompose under these conditions. If the melting point exceeds 95 degrees Celsius then it is most preferred to use a solvent. Suitable solvents are alcohols containing 1 to 5 carbon atoms and most preferably those containing 1 to 3 carbon atoms, that is to say methanol, ethanol, n-propanol or isopropanol. If the compound of formula II is an alkoxy silane, then most preferably the alkoxy group of the solvent alcohol will be the same as the alkoxy group of the alkoxy silane. For example, if the compound of formula II is a methoxy silane, then the preferred solvent is methanol. The concentration of the compound in the solvent may be from 10 to 90 percent by weight and most preferably between 25 and 75 percent by weight and most preferably 50% by weight. The solution is prepared and added to the slurry at a temperature between a lower limit of 0 degrees Celsius and an upper limit which is at least 10 degrees below the boiling point of the solvent or 95 degrees Celsius, or the temperature of the slurry, whichever is lower.

After the addition of the hydrophobic compound of formula II it is desirable to calculate the equivalent balance (EB) of the compound of formula II prior to determining how much if any mineral acid or alkali metal hydroxide (or solutions thereof) to add. The equivalent balance (EB) may be determined from the absolute value of the sum of the group values of X, R^{15} , R^{16} and R^{17} and the weight added, and the molecular weight of the compound, according to the following scheme: The group contribution of X for either X=Cl or X=Br is

-1, thus if X is present it is given a value of -1. The group contribution of each of R^{15} , R^{16} and R^{17} is generally zero for all groups except as follows: if the group is $\text{CH}_3\text{COO}^\ominus$, Cl^\ominus or Br^\ominus , in which case it is -1, or if it is amino, ONa, OK, or OLi in which case it is +1. If the sum of the group contributions for X, R^{15} , R^{16} and R^{17} is zero, then no adjustment with mineral acid or alkali metal hydroxide (or solutions thereof) is necessary. If the sum of the group values is a positive integer, then adjustment with mineral acid is necessary, and if it is negative, then adjustment with alkali hydroxide is indicated.

For example, where $R^{15}=\text{OC}_2\text{H}_5$, $R^{16}=\text{OCH}_3$, $R^{17}=\text{CH}_3$ and $\text{X}=\text{Cl}$, the sum Σ of the group values (g.v.) is:

$$\begin{aligned}\Sigma &= (\text{g.v. OC}_2\text{H}_5) + (\text{g.v. OCH}_3) + (\text{g.v. CH}_3) + (\text{g.v. Cl}) = \\ & (0) + (0) + (0) + (-1) = -1.\end{aligned}$$

The negative sign in front of the sum indicates adjustment with alkali metal hydroxide is required. The number of equivalents of alkali required is given by the equivalent balance (EB) which includes the absolute value of the sum of the group contributions ($|\Sigma|$) as a scaling factor.

$$\text{EB} = \frac{|\Sigma| \times \text{weight in grams of the compound added}}{\text{molecular weight of the added chemical.}}$$

In continuing the example, if the hydrophobicizing process were scaled so as to require 3450 grams of a compound of formula II with a molecular weight of 466 grams and the sum of the group values gave -1, then EB would be calculated as follows:

$$\text{EB} = |-1| \times 3450/466 = 7.4 \text{ gram-equivalents.}$$

It would be required in this example to add 7.4 gram-equivalents of alkali metal hydroxide. Sodium hydroxide is the preferred alkali metal hydroxide. The weight of sodium hydroxide required would be:

$$\text{Weight} = (\text{EB}) \times (\text{Equivalent Weight of NaOH}) = 7.4 \times 40.0 = 296 \text{ grams.}$$

10 The preferred technique is to dissolve the alkali hydroxide or mineral acid in water so as to obtain a concentration between 5 and 25% by weight and most preferably between 5 and 10% by weight prior to adding the solution to the slurry. The temperature of the solution may be from 0 degrees Celsius to 100 degrees Celsius under atmospheric pressure, or if a pressure vessel is used for preparation of the solution then it may be from 0 degrees Celsius to 130 degrees Celsius. It is preferred that the temperature of the solution be within 10 degrees of the solution of the slurry. The dispersion of the solution in the slurry is effected by mixing.

20 The hydrophobicizing process described thus far provides an aqueous slurry or dispersion of hydrophobicized silica, which can be used as such or can be filtered and dried. In a preferred embodiment the slurry is mixed with a hydrocarbon or other solution of either vinyl solution SBR or high cis polybutadiene, provided that the solvent is immiscible with, or mostly immiscible with water, to form a preblend. The elastomer solutions may be made by dissolving the respective solid elastomer in a solvent, or they may be

solutions resulting from the polymerisation of monomers in the solvent. Optionally, processing oil and antioxidants may be added to the hydrocarbon solutions prior to mixing with the slurry, or they may be added after mixing the slurry and the elastomer solutions.

The following examples are provided by way of illustration, and are intended in no way to limit the scope of the invention.

EXAMPLES

10 General Remarks

The abbreviation "phr" represents "parts per hundred parts rubber". "Parts" represents parts per 100 parts rubber. The terms "rubber" and "polymer" are used interchangeably.

The vinyl solution styrene butadiene used was based on a commercial grade Buna VSL 5025-1 (formerly Buna VSL 1950S25 available from Bayer). This is a co-polymer of styrene and butadiene, the styrene content being about 25% and the vinyl content of the butadiene portion being about 67%, this grade further contains about 37.5 parts per 100 parts of
20 total polymer of highly aromatic oil. To the above polymer was added 80 parts, per 100 parts of total polymer of silica hydrophobicized by the above described method of Canadian application number 2,205,789 using 4.0 parts per 100 of total polymer of N-oleyl-N-(3-trimethoxysilyl) propylamine, and with 6.4 parts per 100 of total polymer of the silane coupling agent Si69; for a total of 228.0 parts per 100 parts of polymer. The resulting silica masterbatch product was given

the designation XQ209.

The high cis polybutadiene rubber used was based on a commercial grade Taktene 1203 (available from Bayer) which has a cis content of about 96%. To this polymer was added 80 parts by weight per 100 parts of total polymer, of silica hydrophobicized as described above using 4.0 parts per 100 of polymer of N-oley1-N-(3-trimethoxysilyl) propylamine and 6.4 parts per 100 of polymer of the silane coupling agent Si69, mixed with 30 parts by weight per 100 parts of polymer of highly aromatic oil; for a total of 220.4 parts per 100 parts of polymer. The resulting silica masterbatch product was given the designation XQ211.

The above two silica masterbatch polymers were mixed in an internal mixer followed by a mill mix in a ratio of 70 parts by weight per 100 parts of polymer of the XQ209 to 30 parts by weight per 100 parts of polymer of XQ211; other compounding ingredients commonly used in the industry such as zinc oxide, stearic acid, antidegradants, sulfur and accelerators (added on a rubber mill) were also included in the mixture. The resulting compounds were then cured in appropriate test sample shapes by heating at about 166°C for a period of time varying from 10 minutes to 15 minutes depending on the test sample configuration.

Example I

In the following example, compounds "A" and "B" are comparative examples while compounds "C" "D" "E" and "F" are compounds according to the invention by virtue of containing

hydrophobicized silica in the polymer masterbatch form. In this example all the compounds are formulated so as to contain 70 parts by weight per 100 polymer of the vinyl solution SBR (VSL5025-1) and 30 parts per 100 polymer of the high cis polybutadiene (Taktene 1203), a total filler content of 80 parts and a total oil content of 35.3 parts. The black-containing compound "A" contains the frequently used tire tread carbon black N234 available from Cabot Carbon. It is noted that the silica-containing compounds (compounds "B" to "F") all contain the equivalent of 6.4 parts of silane coupling agent Si69 available from Degussa; additionally these compounds contain the accelerator Vulkacit D/C (DPG) available from Bayer which is necessary for the dry mix compound "B" to adequately accelerate the vulcanisation of dry mixed silica compounds and is included in compounds "C" to "F" for purposes of comparison. The XQ209 vinyl solution SBR silica masterbatch was as previously described:

137.5 Buna VSL 5025-1 (100 polymer, 37.7 aromatic oil)

80 Silica

6.4 Si69

4.0 N-oley1-N-(3-trimethoxysilyl)propylamine.

XQ209B is the same composition as XQ209 but was extruded through a drying extruder as part of the drying process.

The XQ211 high cis polybutadiene silica masterbatch was as previously described:

100 Taktene 1203

80 Silica

30 Aromatic process oil

6.4 Si69

4.0 N-oley1-N-(3-trimethoxysilyl)propylamine

XQ211B is the same composition as XQ211 but was extruded through a drying extruder as part of the drying process.

The other ingredients are all common to each compound formulation and are readily available in the industry. The compound formulations are shown in Table 1 below:

TABLE 1

COMPOUND		A VSL5025-1 T1203 Black	B VSL5025-1 T1203 Silica	C XQ209 XQ211 Silica mb	D XQ209 XQ211B Silica mb	E XQ209B XQ211 Silica mb	F XQ209B XQ211B Silica mb
10	Buna VSL 5025-1	1A	96.3	96.3			
	TAKTENE 1203	1A	30	30			
	XQ 209 SSBR (J-09093)	1A			159.6	159.6	
	XQ209B SSBR (J-09092)	1A				159.6	159.6
	XQ 211 BR (J-09094)	1A			66.1		
	XQ 211B BR (J-09095)	1A				66.1	66.1
	N 234 Carbon Black	1B	80				
	HI-SIL 233	1B		80			
	SILANE Si-69	1B		6.4			
	STEARIC ACID	1B	1	1	1	1	1
	SUNDEX 790	1B	9	9			
	SUNPROOF IMPROVED WAX	1B	1.5	1.5	1.5	1.5	1.5
	VULKANOX 4020 (6PPD)	1B	1	1	1	1	1
	VULKANOX HS/LG (TMQ)	1B	1	1	1	1	1
	ZINC OXIDE (KADOX 920)	1B	2.5	2.5	2.5	2.5	2.5
	SULFUR NBS	1C	1.4	1.4	1.4	1.4	1.4
	20	VULKACIT CZ/EG-C (CBS)	1C	1.7	1.7	1.7	1.7
VULKACIT D/C (DPG)		1C		2	2	2	2
TOTAL		225.4	233.8	237.8	237.8	237.8	237.8
Specific Gravity		1.148	1.190	1.189	1.189	1.189	1.189

Hi-Sil 233 is a silica supplied by PPG Industries Inc.

Sundex 790 is an aromatic process oil supplied by Sun Co.

Sunproof Improved Wax is a wax supplied by Uniroyal Chemical.

30 Vulkanox 4020 and Vulkanox HS/CL are antioxidants supplied by Bayer.

Vulkacit CZ/EG-C and Vulkacit D/C are accelerators supplied by Bayer.

In order to prepare vulcanized specimens for testing, the ingredients of the compound formulations shown above were mixed in an internal rubber compound mixer, the particular mixer being a BR-82 Banbury mixer with a volumetric capacity of 1600cc. The mixer settings were:

Speed: 77rpm
Cooling medium set @ 25°C
Ram pressure 30 psi
Start temperature 40°C

10 The mix procedure used for compound A was as follows: the Buna VSL 5025-1 and Taktene 1203 rubbers were first added to the Banbury mixer; after 60 seconds the N234 carbon black, stearic acid, Sundex 790 process oil, wax, Vulkanox 4020, Vulkanox HS and zinc oxide were then added and the ram lowered; after a further 180 seconds the ram was raised and any ingredients that had risen over the ram were swept back into the mass; and finally after a further 60 seconds the mixture was dumped from the Banbury mixer for a total banbury mix time of 5 minutes. The mixture was then transferred to a warm (40°C) two roll mill and 1.4 parts sulfur and 1.7 parts Vulkacit CZ were then blended into the mixture for a mill mix time of four minutes. The nip setting on the mill was then reduced to 0.5 mm and the mixture passed through the mill 6 times in a refining step to give a final mixture whose specific gravity was 1.148.

20 Compound B in the example shown in table 1 was prepared by two mixing steps in the internal mixer with again a final step on a warm mill. The internal mixer settings were the same as used for compound A. The first step to prepare the compound B mixture was to add the vinyl solution styrene rubber containing 100 parts rubber and 37.5 parts of aromatic oil extender Buna VSL 5025-1 and the high cis polybutadiene rubber Taktene 1203 to the internal mixer. This mixture was mixed for

60 seconds. To this mixture 40 parts of untreated silica (Hi-Sil 233) and 3.2 parts of Si-69 silane were added and the mixture mixed for an additional 60 seconds. The ram was then raised and an additional 40 parts of untreated silica and 3.2 parts of Si-69 was added to the mixture. After a further 60 seconds the ram was raised and ingredients that had escaped from the mass were swept back into the mass. The ram was then lowered and mixing continued for a further 60 seconds. The ram was again raised after a total elapsed time of 240 seconds and 10 part stearic acid, 9 parts of Sundex 790 extender oil, 1.5 parts of wax, 1 part of Vulkanox 4020, 1 part Vulkanox HS and 2.5 parts of zinc oxide were added; the ram was swept and then lowered and mixing continued for an additional 60 seconds when the ram was again raised and escaped ingredients swept back into the mass and then lowered and mixing continued for an additional 120 seconds after which the mixture was dumped out of the mixer and formed into a sheet. The total elapsed mixing time for step 1 was 7 minutes.

The internal mixer was then allowed to cool to 40°C and the sheeted out mixture added to the mixer and mixing was 20 continued until the temperature reached 150°C as measured by the ram temperature probe. The total elapsed time for step 2 was 4.5 minutes.

The final mixing step was done on a warm mill to which were added the mixture from internal mixing step 2, 1.4 parts sulfur, 1.7 parts Vulkacit CZ and 2 parts Vulkacit D. This

mixture was blended on the mill for four minutes. The nip setting on the mill was then reduced to 0.5 mm and the mixture passed through the mill 6 times in a refining step to give a final mixture whose specific gravity was 1.190.

10 The mix procedure used for compound C of the formulation as shown in table 1 was prepared by a single mixing step in an internal mixer followed by a final step on a warm mill. The internal mixer settings were the same as used for compound A. The mix procedure was to add to the internal mixer 159.6 parts per hundred rubber of the vinyl solution SBR/silica masterbatch XQ209, 66.1 parts of high cis BR/silica masterbatch XQ211, 1 part of stearic acid, 1.5 parts of wax, 1 part of Vulkanox 4020, 1 part of Vulkanox HS and 2.5 parts of zinc oxide. The ram is then lowered and the mixture is mixed for 180 seconds at which time the ram is raised and any ingredients that have escaped from the mass are swept back into the mixture. The ram is then lowered and the mixture is mixed for a further 60 seconds and then dumped from the mixer. The total elapsed mixing time for this step was 4 minutes.

20 The final mixing step for compound C was done on a warm mill to which was added the mixture from the internal mixer, 1.4 parts per hundred rubber of sulfur, 1.7 parts of Vulkacit CZ and 2 parts of Vulkacit D. This mixture was blended on the mill for 4 minutes. The nip setting on the mill was then reduced to 0.5 mm and the mixture passed through the mill 6 times in a refining step to give a final mixture whose specific gravity was 1.189.

The mix procedure used for compounds D, E and F were the same as used for compound C.

From the mixtures prepared to compound formulations A to F vulcanized test specimens were prepared and tested for physical properties that relate to tire tread performance. The test specimens were vulcanized at a temperature of 166°C for the times as shown on table 2 below.

TABLE 2

COMPOUND	A	B	C	D	E	F
	VSL5025-1 T1203 Black	VSL5025-1 T1203 Silica	XQ209 XQ211 Silica mb	XQ209B XQ211B Silica mb	XQ209B XQ211 Silica mb	XQ209B XQ211B Silica mb
DIN Abrasion						
Vulcanization time (min)	17	23	15	15	15	15
Volume Loss (mm ³)	147	142	120	118	119	123
RSA II TEMP SWEEP						
Cure Time (min)	12	18	10	10	10	10
Cure Temperature: 166°C						
Frequency: 11 Hz						
Temperature Range: -60 to 100°C						
Auto Strain: 0.05%						
Pretension Load: 20g						
Tan delta @ 0°C	0.178	0.234	0.310	0.322	0.303	0.307
ZWICK REBOUND						
Cure Time (min)	17	23	15	15	15	15
Cure Temperature: 166°C						
Resilience @ 100°C (%)	46.0	61.4	65.9	64.9	64.9	66.0
MER 1100 Dynamic Properties						
Frequency: 20Hz @ 60°C						
Load: 7% static+3% dynamic		1.75	1.13	1.05	0.99	1.00
Power Loss (g.m/sec)	3.94	0.155	0.141	0.130	0.136	0.132
Tan Delta	0.299					

The DIN abrasion test was performed according to DIN 53 516. This test measures the volume loss of the test specimen which has been abraded by a 60 grit emery paper. A low value predicts better abrasion resistance of the compound.

The RSA II (Rheometrics Solid Analyzer - version II) test measures the viscoelastic properties of a vulcanized test specimen which is subjected to low sinusoidal strains in tension over a broad temperature. Experience has shown that the tan delta value at zero degrees Celsius, which is the ratio of the loss modulus to the storage modulus, is a good predictor of the tire tread traction properties. A high value predicts better traction properties.

The Zwick Rebound test was performed according to the method ISO 4662. This test when run at 100°C measures the resilience properties of the compound which correlates broadly with the rolling resistance properties of a tire tread compound. A high value predicts lower rolling resistance.

The MER 1100 test measures the viscoelastic properties of a rubber compound by applying a sinusoidal compressive strain on a test specimen. The complex, storage and loss moduli are measured from which are calculated the power loss and tan delta. The test is a good predictor of the rolling resistance characteristics of a tire tread compound. A low value for power loss and tan delta predicts lower rolling resistance.

The results from table 2 indicate that the compounds made using the silica containing masterbatch polymers in which the silica has been hydrophobized have physical properties which will provide improved abrasion resistance, traction and lower rolling resistance properties when compared to the comparative example compounds A and B.

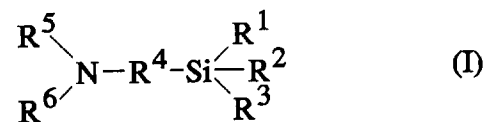
THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An elastomeric composition which comprises
 - 1) a vinyl solution SBR/silica-containing masterbatch, and
 - 2) a high cis polybutadiene/silica-containing masterbatch, wherein the silica has been hydrophobicized.
2. A composition according to claim 1 which comprises from 40 to 90 parts by weight of the vinyl solution SBR portion of the vinyl solution SBR/silica-containing masterbatch and from 60 to 10 parts by weight of the high cis polybutadiene portion of the high cis polybutadiene/silica-containing masterbatch.
3. A composition according to claim 1 or 2 wherein the silica content in the composition is from about 30 to about 100 phr.
4. A composition according to any one of claims 1 to 3, which comprises 25-50 phr aromatic oil.
5. A composition according to any one of claims 1 to 4, wherein component 1) has a styrene content of from about 15 to about 25%, a vinyl content of the butadiene portion of about

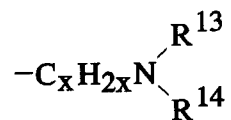
33 to about 73%, and about 25 to about 50 parts, per 100 parts of total polymer, of aromatic oil, and component 2) has a cis content of greater than about 90%, and about 25 to about 50 parts, per 100 parts of total polymer, of aromatic oil.

6. A composition according to claim 1, wherein the silica is hydrophobicized by the following process,

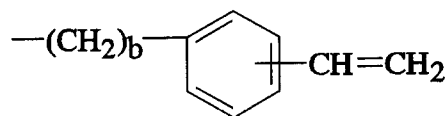
(a) treating silica particles with a compound of formula I



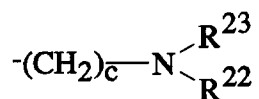
or an acid addition or quaternary ammonium salt thereof, in which at least one of R^1 , R^2 and R^3 , is a hydroxyl group or a hydrolysable group, R^4 is a divalent group that is resistant to hydrolysis at the $\text{Si}-\text{R}^4$ bond, R^5 is hydrogen, a C_{1-30} alkyl or C_{2-30} mono-, di- or triunsaturated alkenyl group, or R^5 is a group of formula



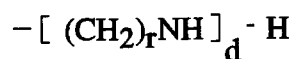
in which x is an integer from 2 to 10, R^{13} and R^{14} are each hydrogen, C_{1-18} alkyl, C_{2-18} mono-, di- or triunsaturated alkenyl, phenyl, a group of formula



wherein b is an integer from 1 to 10, or a group of formula

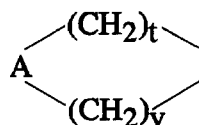


wherein c is an integer from 1 to 10 and R^{22} and R^{23} which may be the same or different, are each hydrogen, C_{1-10} alkyl or C_{2-10} alkenyl, provided that there is no double bond in the position alpha to the nitrogen atom, or a group of formula



wherein r is an integer from 1 to 6 and d is an integer from 1 to 4;

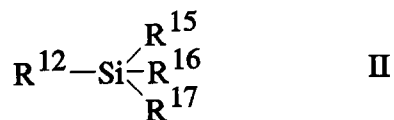
R^6 may be any of the groups defined for R^5 , or R^5 and R^6 may together form a divalent group of formula



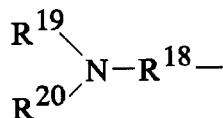
in which A is a -CHR or -NR group in which R is hydrogen or a C_{1-30} alkyl or C_{2-30} alkenyl group, or A is an oxygen or sulfur atom and t and v are each 1, 2, 3 or 4; provided that

the sum of t and v does not exceed 6; and

(b) thereafter adding to the treated silica particles a compound of the formula II



in which R^{15} , R^{16} and R^{17} have the same definitions as R^1 , R^2 and R^3 , defined above and R^{12} is a C_{8-30} alkyl group, a C_{8-30} mono-, di- or triunsaturated alkenyl group, either of which can be interrupted by one or more aryl groups, or a group of formula



or an acid addition or quaternary ammonium salt thereof in which R^{18} is a divalent group resistant to hydrolysis at the $\text{Si}-\text{R}^{18}$ bond, R^{19} is hydrogen, a C_{1-30} alkyl group, a C_{2-30} mono-, di- or triunsaturated alkenyl group, an aromatic group that is substituted by C_{1-20} alkyl or C_{2-20} mono-, di or triunsaturated alkenyl group, and R^{20} may be any of the groups defined for R^{19} , with the provisos that R^{19} and R^{20} do not have a tertiary carbon atom adjacent to the nitrogen atom and that at least one of R^{19} and R^{20} has a carbon chain at least 8 carbon atoms in length uninterrupted by any heteroatom.

7. A composition according to claim 6 wherein the compound of formula I is selected from the group consisting of 3-aminopropylmethyldiethoxysilane, N-2-(vinylbenzylamino)-ethyl-3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, trimethoxysilylpropyldiethylenetriamine, N-2-(aminoethyl)-3-aminopropyltris(2-ethylhexoxy)silane, 3-aminopropyldiisopropylethoxysilane, N-(6-aminoethyl)aminopropyltrimethoxysilane, 4-aminobutyltriethoxysilane, 4-aminobutyldimethylmethoxysilane, triethoxysilylpropyldiethylenetriamine, 3-aminopropyltris(methoxyethoxyethoxy)silane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N-2-(aminoethyl)-3-aminopropyltris(2-ethylhexoxy)silane, 3-aminopropyldiisopropylethoxysilane, N-(6-aminoethyl)aminopropyltrimethoxysilane, 4-aminobutyltriethoxysilane, (cyclohexylaminomethyl)methyldiethoxysilane and N-oleyl-N-(3-trimethoxysilyl) propyl amine or a salt thereof.

8. A composition according to claim 6 wherein the compound of formula II is selected from the group consisting of bis[3-(trimethoxysilyl)propyl]tetrasulfane (Si-168), bis[3-triethoxysilyl)propyl]tetrasulfane (Si-69), bis[2-(triethoxysilyl)ethyl]tetrasulfane (Silquest RC-2), bis[2-(trimethoxysilyl)ethyl]tetrasulfane, bis[2-(triethoxysilyl)ethyl]trisulfane, bis[3-(trimethoxysilyl)propyl]-disulfane, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropylmethyldiethoxysilane, 3-mercaptoethylpropylethoxymethoxysilane, 1,3-bis(3-acryloxypropyl)tetramethoxy-

disiloxane, acryloxypropylmethyldimethoxysilane, 3-methacryloxypropyltrimethoxysilane, allyltrimethoxysilane, diallyldiethoxysilane, 5-(bicycloheptenyl)triethoxysilane, 5-(bicycloheptenyl)methylmethoxyethoxysilane, isopropoxytriacryltitanate, diisopropyldimethacryltitanate, diethoxydi(3-mercaptopropoxy)zirconate, triisopropoxy-(2-mercптоethoxy)zirconate, di[neopentyl(diallyl)oxy]-di(3-mercaptopropoxy)zirconate and N-oleyl-N-(3-trimethoxysilyl)propylamine or a salt thereof.

9. A composition according to any one of claims 6 to 8 wherein N-oleyl-N-(3-trimethoxysilyl)propylamine or a salt thereof is used as the compound of formula I.

10. A composition according to any one of claims 6 to 8 wherein N-oleyl-N-(3-trimethoxysilyl)propylamine or a salt thereof is used as the compound of formula II.

11. A composition according to claim 9 or 10 wherein the salt is N-oleyl-N-(3-trimethoxysilyl)-propyl ammonium chloride.

12. A composition according to any one of claims 1 to 11 which further comprises a coupling agent.

13. A composition according to claim 12 wherein the coupling agent is Si-69.

14. A composition according to any one of claims 1 to 13 in vulcanized form.

15. A composition according to any one of claims 1 to 14 in the form of a tire tread, tire tread hose, hose, industrial drive belt or shoe sole.

16. A composition according to any one of claims 1 to 14 wherein component 1) has a styrene content of about 25%, a vinyl content of the butadiene portion of about 67%, and about 37.5 parts per 100 parts of total polymer of aromatic oil, and component 2) has a cis content of greater than about 90%, and about 30 parts per 100 parts of total polymer of aromatic oil.