

Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to sulfur vulcanizable elastomer composites which are based upon vulcanizable unsaturated polymers and copolymers such as natural rubbers, polyisoprenes, polybutadienes, poly(butadiene-co-styrene), poly(butadiene-co-acrylonitrile) and poly(isobutylene-co-butadiene) and the use of triorganophosphines for enhancing the coupling action of polysulfide coupling agents.

2. Description of the Prior Art

Polysulfide alkoxy silane coupling agents are known, and are described e.g. in U.S. Patents Nos. 3,842,111, 3,873,489, 4,003,843, and 4,044,037. Polysulfide-functional organosilanes are, like mercapto-functional organosilanes, useful as coupling agents in silica-filled and silicate-filled sulfur vulcanizable elastomer composites. However, the polysulfide-functional organosilanes are, as compared to the mercapto-functional organosilanes, less active. Under comparable conditions, the former produce lesser improvements than do the latter in elastomer vulcanizate properties such as tensile modulus.

BRIEF SUMMARY OF THE INVENTION

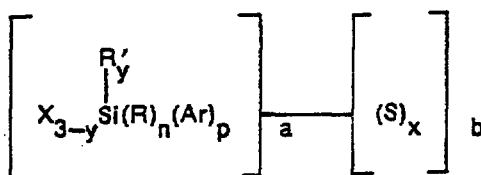
It has now been found that triorganophosphines can be utilized to enhance the coupling action of polysulfide alkoxy silane coupling agents. More specifically, it has been found that compositions which contain triorganophosphine (preferably in admixture with water, lower alkanol, and porous inert inorganic solid carrier) can be utilized to enhance the coupling action of polysulfide alkoxy silane coupling agents in the preparation of vulcanizable rubber from formulations comprising a major proportion of vulcanizable unsaturated polymer or copolymer and a small amount of polysulfide alkoxy silane coupling agent. Also, it has been found that compositions which contain a polysulfide alkoxy silane coupling agent and a triorganophosphine, (preferably in admixture with water, lower alkanol, and porous inert inorganic solid) can be utilized in the vulcanization of sulfur-vulcanizable formulations containing a major proportion of vulcanizable unsaturated polymer or copolymer. The utilization of such compositions improves the elastomer vulcanizate properties as compared to the use of similar compositions without the triorganophosphine.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The sulfur-vulcanizable elastomer composites in which improved coupling action according to the present invention can be obtained are those base upon unsaturated polymers and copolymers such as natural rubbers, polyisoprenes, polybutadienes, poly(butadiene-co-styrene), poly(butadiene-co-acrylonitrile) and poly(isobutylene-co-butadiene).

The preferred sulfur-vulcanizable elastomer composites are those base upon styrene-butadiene copolymers.

The polysulfide alkoxy silane coupling agents which can be employed are known as a class and are described, for example in U.S. Patents Nos. 3,842,111, 3,873,489, 4,003,843, and 4,044,037. A preferred variety of these coupling agents is represented by the formula



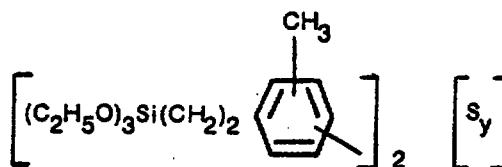
wherein X represents an alkoxy radical, R' represents an alkyl radical having up to 4 carbon atoms, y has a value of from 0 to 2 inclusive, R represents a divalent bridging group selected from alkylene and alkyleneoxy radicals having up to 7 carbon atoms, n has a value of 0 or 1, p has a value of 0 or 1, Ar represents an aryl radical containing from 6 to 12 carbon atoms, (S)_x represents a divalent polysulfide radical each free valence thereof being directly bonded to an aromatic carbon atom of an Ar radical whereby each Ar radical is bonded to another Ar radical through a (S)_x radical, x has a value of from 2 to 6, a has a value of at least 2, b has a value of at least 1, and the ratio of a to b is a value of not more than 2. Illustrative of this preferred variety of coupling agents are the silanes having the formulae



wherein x has an average value of about 4,



and



where y has an average value of about 3. The latter silane is most preferred.

The organophosphines which can be used according to the present invention are those of the formula $\text{R}^1\text{R}^2\text{R}^3\text{P}$, wherein each R represents an organo radical. The preferred organo radicals are alkyl radicals, especially those having up to 8 carbon atoms. Exemplary organophosphines include trimethylphosphine, triethylphosphine, triisopropylphosphine and triheptylphosphine. The most preferred organophosphine is tri-n-butylphosphine.

The organophosphine additive is conveniently utilized in the form of a dry concentrate. One approach is to stir the organophosphine and water in a lower alkanol, e.g. methanol solvent for a few minutes at room temperature, and then to take up the liquid on a porous inert inorganic solid, e.g. calcium silicate, carrier to form a dry concentrate. The dry concentrate can then be added to sulfur-vulcanizable rubber formulations which contain polysulfide silane coupling agent. Another approach is to stir the polysulfide silane coupling agent as well as the organophosphine and water in a lower alkanol, e.g. methanol, solvent for a few minutes at room temperature, and again to take up the liquid on a porous inert inorganic solid, e.g. calcium silicate, carrier to form a dry concentrate. Said dry concentrate can then be added to sulfur-vulcanizable rubber formulations. It is believed that the water supplies protons which reduce the polysulfide linkages. The amount of water utilized will be that necessary to obtain the desired rubber curing rate.

Examples

The specific examples which follow are illustrative of the principles of the invention.

Elastomer Base: A typical elastomer base contains 100 parts by weight of SBR 1502, a styrene-butadiene copolymer (as described in "The Elastomers Manual", International Institute of Synthetic Rubber Producers, 1974 Edition, page 22), 50 parts by weight of precipitated high surface area silica, 8 parts by weight of aromatic hydrocarbon oil, 1.0 parts by weight of tetramethylthiuram monosulfide, 1.5 parts by weight of 2-mercaptobenzothiazole, 2.0 parts by weight of sulfur, 5.0 parts by weight of zinc oxide, 1.0 part by weight of stearic acid, and varying parts by weight of additives according to the present invention.

The elastomer base is processed as follows:

The SBR 1502 is banded on a two-roll 152 ~ 305 mm laboratory rubber mill at a roll temperature of 51°C and is milled for 1 minute, dry concentrates according to the present invention are added and dispersed by further milling for about 2 minutes, half of the silica filler are added followed by the addition of the remaining half along with the aromatic hydrocarbon oil, and these components are dispersed by further milling for 2 to 3 minutes, at which time the remaining (vulcanizing) chemicals are added and dispersed; the mixture so-obtained is removed from the mill as a sheet and is press-vulcanized at 160°C to form. ASTM tensile test sheets. Physical tests of the vulcanizate were performed according to standard ASTM test methods.

Tensile Modulus: Evidence of action by a coupling agent in a composite is manifested through changes in composite physical property values away from the values displayed by the composite in the absence of the agent. Composite properties which may be favorably altered by coupling agent action are many and varied. For example, in elastomeric composites, the effects of coupling agents are seen in terms of increased tensile modulus and abrasion resistance and in decreased hysteresis losses in flexure. In highly extensible elastomeric composites, the measurement of changes in tensile modulus is a particularly useful way of observing coupling effects and has been used extensively in the experimental work described herein. Tensile modulus is defined here as the tensile stress in pounds per square inch of original cross-sectional area necessary to produce a selected extension in a composite specimen, usually 100%, 200% or 300% of the unstressed length; these parameters are usually indicated as M100, M200, or M300, respectively.

Example: Silane/Phosphine Additive

In this Example, additives compositions as indicated were added to the Elastomer Base described above (the values given are in parts per 100 parts SBR 1502):

Additive	1	2	3	4
$\left[(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_2 \text{C}_6\text{H}_4 \right]_2 \left[\text{S}_3 \right]$	0	1.5	1.5	1.5
Tri-n-butylphosphine	0	0	0	1.8
microporous synthetic calcium silicate	0	0	3.5	3.5
Methanol	0	0	3.0	3.0
Water	0	0	0.2	0.2

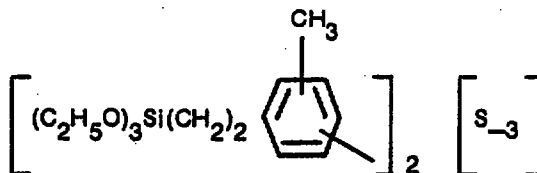
The ASTM test results were:

Vulcanizate	1	2	3	4
Hardness (Shore A)	60	60	60	65
M100 N/cm ²	86.25	120.75	120.75	155.25
M300 N/cm ²	172.50	345	345	690
Tensile N/cm ²	1518	2139	2070	1518
Elongation %	1000	800	800	500
C Tear N/cm ²	138	207	207	207

It is evident that the use of an organophosphine according to the present invention results in a significant and unexpected increase in the tensile moduli (e.g. M100 and M300) of vulcanizates embodying it.

Example: Phosphine Additive

In this Example, 1.5 parts per 100 parts SBR 1502 of a polysulfide silane coupling agent,



was added to the Elastomer Base described above (except in the Control Run, 1) prior to the addition of the indicated amounts of the other additives (the values given are in parts per 100 parts SBR 1502):

Additive	1	2	3	4	5	6	7
5 Tri-n-butyl-phosphine	0	0	0.4	0.8	1.2	1.6	2.0
Microporus synthetic calcium silicate	0	0	0.4	0.8	1.2	1.6	2.0
10 Methanol	0	0	0.38	0.76	1.14	1.52	1.90
Water	0	0	0.01	0.04	0.06	0.08	0.10

15 The ASTM test results were:

Vulcanizate	1	2	3	4	5	6	7
20 Hardness (Shore A)	60	65	65	65	65	65	70
M100 N/cm ²	86.25	138	155.25	155.25	172.50	189.75	189.75
M300 N/cm ²	172.50	414	483	552	655.5	621	621
25 Tensile N/cm ²	1518	2001	1863	1725	1656	1518	1518
Elongation %	1000	700	650	600	550	550	550
30 C Tear N/cm ²	138	207	207	207	207	207	207

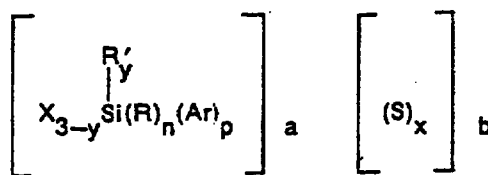
It is again evident that the use of an organophosphine according to the present invention results in a significant increase in the tensile moduli (e.g. M100 and M300) of vulcanizates embodying it.

35 Claims

1. The use of a triorganophosphine of the formula $R^1R^2R^3P$, wherein each of R^1 , R^2 and R^3 represents an alkyl radical having up to 8 carbon atoms for improving the coupling effectivity of polysulfide alkoxy silane coupling agents for the vulcanisation of elastomers in the presence of an inert porous inorganic filler.

40 2. The use of the triorganophosphines according to claim 1 in the form of a concentrate containing the triorganophosphines, water, lower alkanol and inert porous inorganic filler.

3. The use of the concentrate of claim 2 containing additionally a polysulfide alkoxy silane coupling agent of the formula



wherein X represents an alkoxy radical, R' represents an alkyl radical having up to 4 carbon atoms, y has a value of from 0 to 2, R represents a divalent bridging group selected from alkylene and alkyleneoxy radicals having up to 7 carbon atoms, n has a value of 0 or 1, p has a value of 0 or 1, Ar represents an aryl radical containing from 6 to 12 carbon atoms, $(S)_x$ represents a divalent polysulfide radical each free valence thereof being directly bonded to an aromatic carbon atom of an Ar radical whereby each Ar radical is bonded to another Ar radical through a $(S)_x$ radical, x has a value of from 2 to 6, a has a value of at least 2, b has a value of at least 1, and the ratio of a to b is a value of not more than 2.

4. The use of the concentrate of claim 3 wherein the polysulfide alkoxy silane coupling agent is that of the formula

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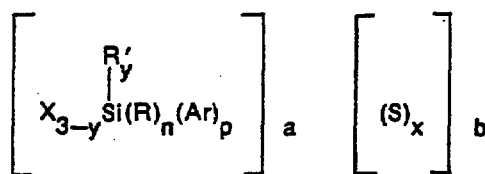
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35 Claims

1. The use of a triorganophosphine of the formula $R^1R^2R^3P$, wherein each of R^1 , R^2 and R^3 represents an alkyl radical having up to 8 carbon atoms for improving the coupling effectivity of polysulfide alkoxy silane coupling agents for the vulcanisation of elastomers in the presence of an inert porous inorganic filler.

40 2. The use of the triorganophosphines according to claim 1 in the form of a concentrate containing the triorganophosphines, water, lower alkanol and inert porous inorganic filler.

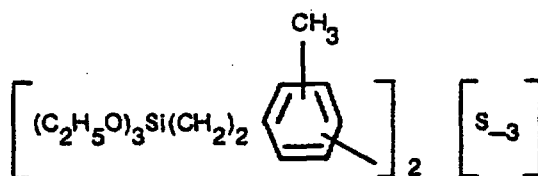
3. The use of the concentrate of claim 2 containing additionally a polysulfide alkoxy silane coupling agent of the formula



45 wherein X represents an alkoxy radical, R' represents an alkyl radical having up to 4 carbon atoms, y has a value of from 0 to 2, R represents a divalent bridging group selected from alkylene and alkyleneoxy radicals having up to 7 carbon atoms, n has a value of 0 or 1, p has a value of 0 or 1, Ar represents an aryl radical containing from 6 to 12 carbon atoms, $(S)_x$ represents a divalent polysulfide radical each free valence thereof being directly bonded to an aromatic carbon atom of an Ar radical whereby each Ar radical is bonded to another Ar radical through a $(S)_x$ radical, x has a value of from 2 to 6, a has a value of at least 2, b has a value of at least 1, and the ratio of a to b is a value of not more than 2.

50 4. The use of the concentrate of claim 3 wherein the polysulfide alkoxy silane coupling agent is that of the formula





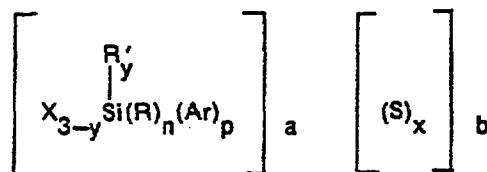
5. The use of the concentrate as in claim 1 in which the triorganophosphine is that of the formula (n-C₄H₉)₃P.

Patentansprüche

1. Verwendung eines Triorganophosphins der Formel R¹R²R³P, in der jedes R¹, R² und R³ eine Alkylgruppe mit bis zu 8 Kohlenstoffatomen bedeutet, zur Steigerung der Kupplungswirksamkeit von Alkoxysilanpolysulfid-Kupplungsmitteln für die Vulkanisation von Elastomeren in Gegenwart eines inerten porösen anorganischen Füllstoffes.

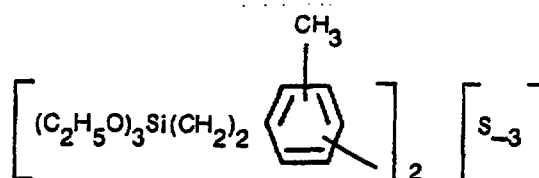
2. Verwendung der Triorganophosphine nach Anspruch 1 in Form eines Konzentrats, enthaltend die Triorganophosphine, Wasser, einen niederen Alkohol und einen inerten porösen anorganischen Füllstoff.

3. Verwendung des Konzentrats nach Anspruch 2, enthaltend zusätzlich ein Alkoxysilanpolysulfid-Kupplungsmittel der Formel



in der X einen Alkoxyrest bedeutet, R' einen Alkylrest mit bis zu 4 Kohlenstoffatomen bedeutet, y einen Wert von 0 bis 2 hat, R eine zweiwertige verbindende Gruppe, ausgewählt aus Alkyl- und Alkylenoxyresten mit bis zu 7 Kohlenstoffatomen ist, n einen Wert von 0 oder 1 hat, p einen Wert von 0 oder 1 hat, Ar einen Arylrest bedeutet, der 6 bis 12 Kohlenstoffatome enthält, (S)_x einen zweiwertigen Polysulfidrest bedeutet, bei dem jede freie Wertigkeit unmittelbar an ein aromatisches Kohlenstoffatom eines Ar-Restes gebunden ist, wodurch jeder Ar-Rest über eine (S)_x-Gruppe an einen anderen Ar-Rest gebunden ist, x einen Wert von 2 bis 6 hat, a einen Wert von mindestens 2 hat, b einen Wert von mindestens 1 hat und das Verhältnis von a zu b nicht mehr als 2 beträgt.

4. Verwendung des Konzentrats des Anspruchs 3, bei dem das Alkoxysilanpolysulfid-Kupplungsmittel der Formel



entspricht.

5. Verwendung des Konzentrats nach Anspruch 1, bei dem das Triorganophosphin der Formel (n-C₄H₉)₃P entspricht.

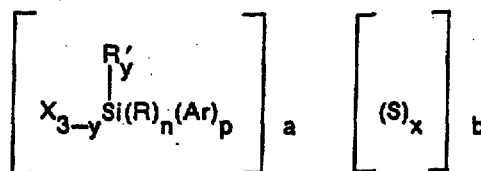
Revendications

1. Utilisation d'une triorganophosphine de formule R¹R²R³P, dans laquelle chacun de R¹, R² et R³ représente un radical alkyle ayant jusqu'à 8 atomes de carbone, pour améliorer l'efficacité de couplage d'agents de couplage du type polysulfure d'alkoxysilane pour la vulcanisation d'élastomères en présence d'une charge inorganique poreuse inerte.

2. Utilisation des triorganophosphines suivant la revendication 1, sous la forme d'un concentré contenant les triorganophosphines, de l'eau, un alcool inférieur et une charge inorganique poreuse inerte.

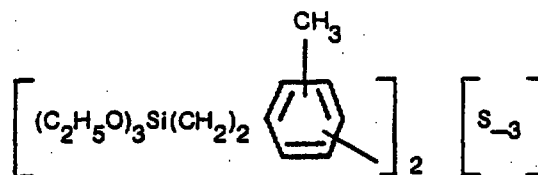
3. Utilisation du concentré de la revendication 2, contenant en outre un agent de couplage du type polysulfure d'alkoxysilane, de formule





dans laquelle X représente un radical alkoxy, R' représente un radical alkyle ayant jusqu'à 4 atomes de carbone, y a une valeur de 0 à 2, R représente un groupe de pontage divalent choisi entre des radicaux alkylène et alkylèneoxy ayant jusqu'à 7 atomes de carbone, n a une valeur de 0 ou 1, p a une valeur de 0 ou 1, Ar représente un radical aryle contenant 6 à 12 atomes de carbone, (S)_x représente un radical polysulfure divalent dont chaque valence libre est liée directement à un atome aromatique de carbone d'un radical Ar, chaque radical Ar étant lié à un autre radical Ar par l'intermédiaire d'un radical (S)_x, x a une valeur de 2 à 6, a a une valeur d'au moins 2, b a une valeur d'au moins 1 et le rapport de a à b a une valeur qui ne dépasse pas 2.

4. Utilisation du concentré suivant la revendication 3, dans lequel l'agent de couplage du type polysulfure d'alkoxysilane répond à la formule



5. Utilisation du concentré suivant la revendication 1, dans lequel la triorganophosphine est celle qui répond à la formule (n-C₄H₉)₃P.

