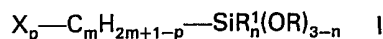


- (21) Application No **8026114**
(22) Date of filing **11 Aug 1980**
(30) Priority data
(31) **2933345**
(32) **17 Aug 1979**
(33) **Fed. Rep. of Germany (DE)**
(43) Application published
18 Mar 1981
(51) **INT CL³**
C08K 5/54 C08J 3/24
(52) Domestic classification
C3K 221 222 230 GC
C3W 202 202C 203 208
209 212 213 213C
C3Y B100 B212 B215
B262 B263 B270 B288
B289 B500 G300
(56) Documents cited
GB 2020293A
GB 1297210
GB 1289083
GB 655612
(58) Field of search
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C3V
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(54) **Vulcanisable rubber mixture**

(57) The mixture comprises halogen-free rubber or a mixture of such rubber with at most 80%, based on the total weight of the rubber, of a halogen-containing rubber; a silicate filler; a vulcanisation accelerator; and at least one organo silane of the formula



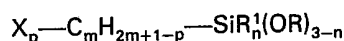
in which X represents chlorine or bromine, p is 1 or 2, m is 1 to 5, R¹ represents a C₁-C₅-alkyl group, a

C₅-C₈-cycloalkyl group or a phenyl group, R represents a C₁-C₅-alkyl group, a C₅-C₈-cycloalkyl group, a methoxyethyl group, a phenyl group or the benzyl group and n is 0, 1 or 2, or a hydrolysate and/or condensate thereof. Other auxiliaries such as metal oxides, carbon black, sulphur (donors), fatty acids, stabilisers and inhibitors may be included and the mixture may additionally contain certain sulphur-containing organo silanes. The mixtures are useful in the production of tyres, tyre treads, industrial rubber products and shoe soles.

SPECIFICATION

Vulcanisable rubber mixture

- This invention relates to formable and vulcanisable rubber mixtures based on halogen-free rubbers which, apart from the rubber that does not contain any halogen in the molecule, contain as their main constituents a silicate filler, optionally in admixture with the filler carbon black, optionally sulphur and/or sulphur donors, at least one vulcanisation accelerator and at least one organosilane containing at least one alkoxy silyl group. 5
- It is known that the use of silica fillers instead of carbon black in rubber mixtures based on so-called all-purpose rubbers (AP-rubbers in short, i.e. rubbers which have been widely used for most well known applications such as, in particular, styrene-butadiene rubber, butadiene rubber, butadiene-acrylonitrile rubber and natural rubbers) is limited for the following three property-related reasons: 10
1. In AP-rubbers, silica fillers comparable in their specific surface to the carbon blacks produce higher Mooney viscosities than carbon blacks.
 2. Silica fillers adversely affect the vulcanisation kinetics and the crosslinking yield of accelerated sulphur vulcanisation as preferably used for AP-rubbers. 15
 3. In rubber mixtures and vulcanisates, silica fillers have smaller rubber-active surfaces which is clearly reflected in reduced performance, particularly in regard to wear resistance.
- It is known that these significant disadvantages can be overcome by using organosilanes in rubber mixtures filled with silica fillers. Organosilanes of this type are required to be "bifunctional", i.e. they must have firstly a filler-active function, which is normally performed by alkoxy silyl groups, and secondly a rubber-active function which is normally performed by sulphur-containing groups, such as $\text{—S}_x\text{—}$ ($x = 2$ to 6) groups and —SH groups. The —SH groups clearly take part in the accelerated sulphur vulcanisation reaction. 20
- Suitable organosilanes are, for example, the eminently suitable bis-(alkoxysilylalkyl)-oligosulphides, such as for example bis-(triethoxysilylpropyl)-tetrasulphide (DE-PS No. 22 55 577). An alternative to the separate addition of silicate fillers and silanes to the rubber mixtures is to mix the substances in question beforehand (US-PS No. 3,997,356). Silica-containing vulcanisates are formed in this way and, even in highly stressed articles such as tyre treads, perform as well as carbon black. The disadvantage of the compounds mentioned above is that their production involves several steps, i.e. high technical outlay which is reflected in corresponding high prices. 25 30
- A crosslinkable rubber mixture containing oligosulphidic organosilanes, known vulcanisation accelerators and—as filler—a silicate filler, but no elemental sulphur is also known (BE-PS No. 832,970 or DE-PS No. 25 36 674). The crosslinking reaction carried out with this mixture may be referred to in simple terms as "sulphur-free silane crosslinking". 35
- Mercapto silanes, such as 3-mercaptopropyl trimethoxy silane, vinyl silanes, such as vinyl trimethoxy silane, and aminosilanes, such as 3-aminopropyl triethoxy silane, have also become known for mixtures based on SBR- and EPDM- rubbers (Rubber World, October 1970, pages 54 and 55).
- Silicate-filled rubber mixtures based on the selected group of halogen-containing rubbers have also been proposed, the mixtures in question containing *inter alia* certain readily obtainable and freely available halogen-containing silanes. It was surprisingly found that these mixtures give extremely valuable vulcanisation products. 40
- It was even more surprising to find that, even in rubber mixtures based on rubbers which do not contain any halogen bound in the molecule, the same simple halogen-containing silanes favourably influence the vulcanisation process or rather the crosslinking kinetics and make it possible to obtain vulcanisates of which the properties are particularly valuable and, in some cases, may be described as outstanding such as, for example, the elasticity properties as determined, for example, by the compression set test. 45
- The present invention provides a vulcanisable rubber mixture of at least one vulcanisable halogen-free rubber or of a mixture of one or more halogen-free rubbers with at most 80%, based on the total weight of the rubber, of at least one halogen-containing rubber; at least one silicate filler in quantities of from 1 to 250 parts by weight, at least one oxide of the metals zinc, magnesium and lead in quantities of from 0 to 15 parts by weight; at least one monobasic fatty acid containing from 12 to 24 carbon atoms in the alkyl chain, benzoic acid or salicylic acid in quantities of from 0 to 10 parts by weight; optionally sulphur and/or sulphur donors in quantities of from 0.1 to 15 parts by weight; at least one vulcanisation accelerator in quantities of from 0.1 to 10 parts by weight; at least one plasticiser in quantities of from 0 to 100 parts by weight; at least one stabiliser from the group comprising anti-agers, anti-fatigue agents, oxidation inhibitors, light stabilisers and anti-ozonants in respective quantities of from 0 to 10 parts by weight; carbon black in quantities of from 0 to 150 parts by weight; optionally other standard rubber auxiliaries in the usual quantities and at least one organosilane, the rubber mixture containing as organosilane from 0.1 to 20 parts by weight of at least one compound corresponding to the general formula 50 55 60



in which X represents chlorine or bromine, p is 1 or 2, m is 1 to 5, R¹ represents a C₁—C₅-alkyl group, a C₅—C₈-cycloalkyl group or a phenyl group, R represents a C₁—C₅-alkyl group, a C₅—C₈-cycloalkyl group, a methoxyethyl group, a phenyl group or a benzyl group and n is 0, 1 or 2, or a hydrolysate and/or a condensate thereof, all the quantities specified being based on 100 parts by weight of the rubber.

- 5 Preferably the rubber mixture additionally contains—per 100 parts by weight of rubber—from 0.5 to 10 parts by weight of at least one organosilane corresponding to the following formulae 5



and/or



- 10 in which R and R¹, which may be the same or different, each represent an alkyl group containing from 1 to 4 carbon atoms, a cycloalkyl group containing from 5 to 8 carbon atoms or a phenyl radical, n is 0, 1 or 2, Alk represents a difunctional, straight-chain or branched hydrocarbon radical containing from 1 to 10 carbon atoms and x is a number of from 2.0 to 8.0 or a hydrolysate and/or a condensate thereof. 10
- The halogen alkyloxy silanes I, which according to the invention must be present in the diene rubber mixtures in quantities of from 0.1 to 20 parts by weight and preferably in quantities of from 1 to 15 parts by weight, based on 100 parts by weight of the rubber, include in particular the following silanes, chloromethyl trimethoxy silane, chloromethyl triethoxy silane, bromomethyl triethoxy silane, dichloromethyl triethoxy silane, 1-chloro-1-methyl methyl trimethoxy silane, 2-chloroethyl trimethoxy silane, 2-bromoethyl trimethoxy silane, 2-dibromoethyl trimethoxy silane, 3-bromopropyl trimethoxy silane, 3-chloropropyl trimethoxy silane, 3-dichloropropyl trimethoxy silane, 3-chloropropyl triethoxy silane, 3-bromopropyl triethoxy silane, 3-dibromopropyl triethoxy silane, 2-bromo-1-methyl ethyl tripropoxy silane, 2-dichloroethyl tri-n-butoxy silane, 2-chloroethyl tri-2'-methyl propoxy silane, 3-bromopropyl tri-t-butoxy silane, 3-dibromopropyl-triisopropoxy silane, 3-bromopropyl tri-n-pentoxy silane, 2-chloroethyl tri-2'-ethyl ethoxy silane, 2-bromo-2-methyl ethyl dimethoxy ethoxy silane, 3-dichloropropyl methoxy ethoxy propoxy silane, 3-chloropropyl dimethoxy methyl silane, 3-bromopropyl diethoxy ethyl silane, 3-chloropropyl ethoxy diethyl silane, 3-bromopropyl tris-(1'-methoxyethoxy)-silane, 3-chloropropyl diethoxy phenyl silane, 3-dichloropropyl dimethoxy cyclopentyl silane, 3-bromopropyl di-n-propoxy cyclohexyl silane, 3-chloropropyl dicyclohexoxy cyclohexyl silane, 3-bromopropyl diethoxy cycloheptyl silane, 3-chloropropyl ethoxy phenyloxy ethyl silane, 3-dibromopropyl benzyloxy ethoxy ethyl silane, 4-chloro-n-butyl trimethoxy silane, 4-bromobutyl trimethoxy silane, 3-chloro-2-methyl propyl trimethoxy silane, 3-chloro-3-methyl propyl cyclooctyl dipropoxy silane, 3-chloro-2-ethyl propyl diethoxy methyl silane, 3-bromo-3-ethyl propyl dimethoxy methyl silane, 3-chloro-2-methyl propyl dimethoxy phenyl silane, 5-chloro-n-pentyl triethoxy silane, 4-bromo-1-methyl butyl cyclooctoxy dimethoxy silane, 4-bromo-2-methyl butyl triethoxy silane, 2-chloro-2-methyl ethyl tripentoxy silane, 2-dichloro-2-methyl ethyl tributyl silane, 3-bromopropyl triphenoxy silane, 3-chloropropyl tribenzyloxy silane, 3-dibromopropyl tricyclopentoxy silane and 3-bromopropyl tri-n-pentoxy silane. It is preferred to use halogen alkoxy silanes containing one halogen atom (p is 1 in formula I) and three alkoxy silyl groups. 15
- The silanes of formula I containing two halogen atoms include in particular dibromomethyl triethoxy silane, dichloromethyl triethoxy silanes, 2-dichloroethyl triethoxy silane, 2-dibromoethyl tri-n-propoxy silane, 3-dichloropropyl triethoxy silane, 2-dichloro-i-propyl triethoxy silane, 2-dibromo-i-propyl tri-i-propoxy silane, 3-dichloropropyl tri-n-propoxy silane, 3-dibromopropyl tri-n-butoxy silane, 4-dichlorobutyl triethoxy silane, 4-dibromobutyl tri-n-propoxy silane, 5-dichloropentyl triethoxy silane, 5-dibromopentyl tri-n-propoxy silane and mixtures thereof. 20
- 45 The silanes corresponding to formulae I, II and III may be replaced by their hydrolysates and condensates, optionally in part, i.e. by mixtures of the non-hydrolysed or non-condensed silanes with the hydrolysed and/or condensed silanes. Neither hydrolysis nor condensation has to be complete, so that partial hydrolysates or partial condensates may also be used in accordance with the invention. These partial hydrolysates or partial condensates are possible because the silanes contain (see formula II) or may contain (see formulae I and III) several oxysilyl groups in the molecule. 25
- The condensates include in particular the condensates of the silanes with alcohols, preferably dihydric alcohols such as, for example, ethylene glycol, propylene glycol, trimethylene glycol, trimethyl ethylene glycol, tetramethylene glycol, pentamethylene glycol, etc., diethylene glycol, butane diols such as 1,4-butane diol, dipropylene glycol, polyethylene glycols and glycidol (2,3-epoxy-1-propanol). 30
- 55 The hydrolysis and condensation reactions are carried out in known manner. They lead to compounds of higher molecular weight with for example higher boiling points etc., which can be of advantage in the production of the rubber mixtures according to the invention. 35
- Silanes corresponding to formula I are produced in known manner, for example from halogen silanes still containing at least one hydrogen atom, by catalytically controlled addition with a 60 halogenated hydrocarbon containing a C—C-double bond (hydrolysis). The halogen atom (s) situated on the silicon atoms is/are then converted into alkoxy silanes again in known manner, for example, by

alcoholysis. It has been found that the crude silanes may also be successfully used for the purposes of the invention straight from production, providing they are substantially free from hydrolysable halide and hydrogen halide or have been freed therefrom by treatment with ammonia or sodium hydride, optionally followed by rectification.

5 The rubbers which may be used in accordance with the invention include any rubbers which still 5
contain C—C-double bonds, which may be crosslinked with sulphur and vulcanisation accelerator(s) to
form elastomers and which do not contain any halogen in the molecule and mixtures thereof;
particularly so-called diene elastomers. Rubbers of this type are, for example, natural and synthetic
rubbers which may be oil-extended, such as butadiene rubbers, isoprene rubbers, butadiene-styrene
10 rubbers, butadiene-acrylonitrile rubbers, butyl rubbers, terpolymers of ethylene, propylene and 10
unconjugated dienes, carboxyl rubbers, epoxide rubbers and transpolypentenamers.

Rubber blends of the above-mentioned rubbers with other polymers in quantities generally
amounting to at most 80% by weight and preferably to less than 50% by weight, based on the total
weight of the rubber, may also be used in accordance with the invention. Blends such as these include,
15 for example, halogenated butyl rubbers, particularly brominated or chlorinated butyl rubbers, chlorinated 15
rubbers, rubber hydrochlorides and, in particular, the polymers of 2-chloro-1,3-butadiene, also
chlorosulphonated polyethylene ethylene-propylene copolymers, ethylene-vinyl acetate copolymers,
chemical derivatives of natural rubber and modified natural rubbers. It is preferred to use diene rubbers,
EPDM-polymers and their blends.

20 The silicate fillers which may be used in accordance with the invention, optionally in the form of a 20
mixture of two or more fillers, are fillers known *per se* in rubber technology. The term "silicate filler" is a
broad term for fillers which consist of silicates, contain silicates and/or include silicates in the broadest
sense in chemically bound form and which are compatible with rubbers and may be worked into rubber
mixtures.

25 The silicate fillers include in particular highly dispersed silica fillers consisting essentially of silicon 25
dioxide and having specific surfaces of from about 5 to 1000 m²/g and preferably from 20 to 400 m²/g
(as measured by the nitrogen adsorption method described in DIN 66 132) and primary particle sizes in
the range from about 10 to 400 nm which may be produced for example by precipitation, hydrothermal
dissociation, by the hydrolysis and/or oxidation at high temperatures (also known as flame hydrolysis) of
30 volatile silicon halides (pyrogenic silica) or by an arc process. These silica-containing fillers may even be 30
present in the form of mixed oxides or oxide mixtures with the oxides of the metals aluminium,
magnesium, calcium, barium, zinc and/or titanium. They may even have been hydrophobised in known
manner with silanes.

The silicate fillers also include:

35 Synthetic silicates, for example, aluminium silicates or alkaline-earth metal silicates, such as 35
magnesium or calcium silicate, with specific surfaces of from about 20 to 400 m²/g and primary particle
sizes of from about 10 to 400 nm.

Natural silicates, for example, kaolins, clays and asbestoses, also natural silicas, such as for
example quartz and kieselghur.

40 Glass fibres and glass fibre products, such as mats, strands, woven cloths, non-woven structures 40
and the like, also glass microbeads.

The above-mentioned silicate fillers are preferably used in quantities of from 10 parts by weight or
even less up to 250 parts by weight per 100 parts by weight of the rubber polymer.

45 Filler mixtures include silica/kaolin or silica/glass fibres/asbestos and mixtures of the silicate- 45
containing reinforcing fillers with known rubber-quality carbon blacks, for example silica/HAF-carbon
black or silica/glass fibre cord/ISAF-carbon black.

50 Typical examples of the silicate fillers which may be used in accordance with the invention are the 50
silicas or silicates known commercially as AEROSIL, ULTRASIL, SILTEG, DUROSIL, EXTRUSIL, CALSIL
and the hydrophobised silica fillers AEROSIL R 972 and SIPERNAT D 17 which are all manufactured and
marketed by DEGUSSA.

According to the invention, preferred silicate fillers are the above-mentioned highly disperse or
active silicas, particularly the precipitated silicas, which are preferably used in quantities of from 5 to
150 parts by weight per 100 parts by weight of rubber.

55 The rubber mixtures according to the invention may additionally contain carbon black not only to 55
ensure that the vulcanisates are grey or black in colour, but also to obtain special, valuable vulcanisate
properties, the known rubber-grade carbon blacks being preferred. The carbon black is used in
quantities of from 0 to 150 parts by weight, based on 100 parts by weight of rubber, in the new rubber
mixtures.

60 Carbon blacks such as these include the rubber-grade carbon blacks manufactured by DEGUSSA 60
and commercially available for example under the name of CORAX.

Where silicate filler and carbon black are simultaneously present in the rubber mixtures, the total
filler content, based on 100 parts by weight of rubber, is limited to at most 300 parts by weight and
preferably to at most 150 parts by weight.

65 In the context of the invention, a lower limit denoted by the number zero means that the 65
constituent of the mixture may, but does not have to be, present in the rubber mixture. Accordingly, if

for example carbon black is present in a mixture, the lower limit should in practice be put at 0.05 part by weight.

It has proved to be of particular advantage in practice to mix one or more halogen silanes corresponding to formula I (or a hydrolysate and/or condensate thereof)—before they are worked into the constituents of the rubber mixture—with the required silicate filler and/or the carbon black, for example, with an HAF-carbon black of the N 330 type (specific surface according to DIN 66 132 78 m²/g; mean primary particle size 27 nm; dibutyl phthalate absorption according to DIN 53 601 100 ml/100 g) or with a silica filler (specific surface between 160 and 190 m²/g; mean primary particle size 18 nm), i.e. to prepare a master batch of one or more of the silanes and filler and further to process the master batch with the constituents or with certain constituents of the mixture. Master batches of this type are preferably 1:1 (by weight) mixtures of halogen silane and filler such as, for example, a mixture, preferably of equal parts by weight, of 3-chloropropyl triethoxy silane and/or a hydrolysate and/or condensate thereof, and precipitated silica filler or carbon black or silica filler and carbon black. Silica fillers of the type in question, particularly highly disperse silica fillers having specific surfaces of from about 100 to 250 m²/g, are described above as are the carbon blacks. The carbon blacks processed in the rubber industry are particularly preferred.

It is also advantageous to prepare a master batch of at least one organosilane of formula II and/or III, a hydrolysate and/or condensate or the organosilane of formula II and/or III and a silica filler obtained by precipitation in aqueous medium and/or carbon black. For example, a master batch of at least one bis-(3-triethoxysilylpropyl)-oligosulphide containing from 2 to 8 sulphur atoms in the molecule, its hydrolysate and/or condensate, at least one silica filler obtained by precipitation in aqueous medium with a specific surface (as measured in accordance with DIN 66 132) of from about 100 to 250 m²/g and/or at least one carbon black. The master batch of silane, its hydrolysate and/or condensate and silica filler may additionally contain from 0.2 to 10 parts by weight per 100 parts by weight of silica filler of at least one polyhydric alcohol, for example, ethylene glycol, propylene glycol, diethylene glycol, a polyethylene glycol, glycerol, hexane triol and/or glycidol.

Suitable accelerators or vulcanisation accelerators are the accelerators used in the rubber processing industry which may generally be used for several types of rubber. However, if halogenated rubbers are used, it is also possible to employ special vulcanisation accelerators. Suitable vulcanisation accelerators include the dithiocarbamate, xanthogenate and thiuram accelerators, also the thiazole accelerators, including the mercapto and sulphenamide accelerators, amine accelerators and aldehydeamine accelerators, basic accelerators, including for example the guanidine accelerators and other basic accelerators (see "Vulkanisation und Vulkanisationsmittel", a comprehensive survey by Dr. W. HOFMANN, Leverkusen, Verlag Berliner Union, Stuttgart, 1965, pages 114 *et seq.*, particularly page 122); and—independently of the above classification—the general vulcanisation accelerator classes of mercapto, disulphide, polysulphide, sulphenamide, thiazole and thiourea accelerators.

The thiuram accelerators essentially comprise the tetra-alkyl and dialkyl diaryl thiuram mono, di- and tetrasulphides, such as tetramethyl thiuram monosulphide, tetramethyl thiuram disulphide, tetraethyl thiuram disulphide, dipentamethylene thiuram monosulphide, disulphide, tetrasulphide and hexasulphide, dimethyl diphenyl thiuram disulphide, diethyl diphenyl thiuram disulphide, etc. The dithiocarbamate accelerators are generally derivatives of dialkyl, alkyl cycloalkyl and alkyl aryl dithiocarbamic acids. Two known representatives of this class of accelerators are N-pentamethylene ammonium-N'-pentamethylene dithiocarbamate and the zinc dialkyl dithiocarbamates.

Xanthogenate accelerators are the known derivatives of alkyl and aryl xanthogenic acids, such as for example zinc ethyl xanthogenate.

The mercapto accelerators include in particular 2-mercapto benzthiazole, 2-mercapto imidazoline, mercaptothiazoline and a number of monomercapto- and dimercaptotriazine derivatives (*cf.* for example GB—PS No. 1,095,219). Mercaptotriazine accelerators are, for example, 2-diethanolamino-4,6-bis-mercaptotriazine and 2-ethylamino-4-diethyl amino-6-mercapto-s-triazine.

Disulphide and sulphenamide accelerators are disclosed for example in GB—PS NI. 1,201,862 and include 2-diethylamino-4,6-bis-(cyclohexylsulphenamido)-s-triazine, 2-di-n-propylamino-4,6-bis-(N-tert.-butyl sulphenamido)-s-triazine and, in particular, N-cyclohexyl-2-benzthiazole sulphenamide. The disulphide accelerators include for example bis-(2-ethylamino-4-diethylaminotriazin-6-yl)-disulphide, bis-2-methylamino-4-diisopropylamino-triazin-6-yl)-disulphide and dibenzothiazyl disulphide.

Other sulphidic triazine accelerators are the polysulphidic or oligosulphidic triazine derivatives and their polymers which are produced in accordance with DE—OS No. 20 27 635 and which are also disclosed in GB—PS No. 1,353,532. These accelerators are also sulphur donors.

The aldehyde-amine accelerators include condensation products of saturated or unsaturated aliphatic aldehydes with ammonia or aromatic amines such as, for example, butyraldehyde aniline and butyraldehyde butyl amine. Other basic accelerators are, for example, guanidine derivatives, such as diphenyl guanidine and di-o-tolyl guanidine, also amine accelerators, such as hexamethylene tetramine etc.

The thiourea accelerators include for example thiourea itself and diaryl thioureas, such as 1,3-diphenyl-2-thiourea.

According to the invention, it can be of advantage to use mixtures of two, three or more different accelerators, such as for example disulphidic accelerators, such as di-2-benzothiazyl disulphide, with thiuram accelerators, such as tetramethyl thiuram disulphide, together with sulphur, which may consist completely or partly of insoluble sulphur, or with sulphur donors, such as morpholine disulphide.

5 According to the invention, the accelerators are used in the usual quantities and preferably in quantities of from 0.2 to 10 parts by weight, based on 100 parts by weight of the rubber. 5

Stabilisers known *per se*, particularly those from the group comprising anti-agers, anti-fatigue agents, oxidation inhibitors, light stabilisers and anti-ozonants, and also mixtures thereof, may advantageously be present in the rubber mixtures according to the invention in quantities of from 0.2 to 10 10 parts by weight, based on 100 parts by weight of the rubber. 10

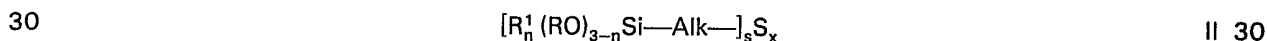
In addition, it is possible to add to the rubber mixtures plasticisers or plasticiser oils, for example highly aromatic naphthenic or paraffinic plasticiser oils, advantageously those having low cold setting points of from about 0°C to -60°C. The quantity in which the plasticiser oil is used may vary within wide limits, amounting to more than 0.5 to 5 parts by weight and more particularly from about 10 to 15 15 about 100 parts by weight, based on 100 parts by weight of rubber. 15

The new rubber mixtures preferably contain an organic acid which is solid at room temperature, of the type used in rubber technology, in quantities of from 0.2 to 10 parts by weight, based on 100 parts by weight of the rubber, preferably a fatty acid, such as stearic acid, palmitic acid, or corresponding acids of the homologous series containing from 12 to 24 carbon atoms in the molecule, also benzoic or 20 20 salicylic acid. 20

In addition, oxides of polyvalent metals, of the type also used in rubber technology, may be added to the rubber mixtures according to the invention in quantities of from 0.1 to 15 parts by weight, based on 100 parts by weight of the rubber.

25 These metal oxides include above all zinc oxide, particularly in finely divided and/or active form. It is also possible to use magnesium oxide or, optionally lead oxide. These oxides are preferably used in finely divided, active or powder form. It is also possible to use mixtures of the metal oxides, particularly where polychlorobutadiene for example is used, as is preferably the case, the above-mentioned metal 25 oxides having a crosslinking effect on this elastomer.

The oligosulphidic organosilanes corresponding to the following formula



in which R and R¹, which may be the same or different, each represent an alkyl group containing from 1 to 4 carbon atoms, a cycloalkyl group containing from 5 to 8 carbon atoms, a methoxyethyl radical or a phenyl radical, n is 0, 1 or 2, Alk represents a difunctional, straight-chain or branched hydrocarbon radical containing from 1 to 10 carbon atoms and x is a number of from 2.0 to 8.0, preferably up to 6.0, 35 35 which may be present in the mixtures according to the invention in quantities of from 0.5 to 10 parts by weight per 100 parts by weight of rubber, are known, for example, from US—PS No. 3,873,489. They are produced by the process described in DE—PS No. 25 42 534 (US Patent No. 4,072,701).

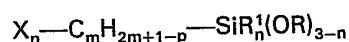
Examples of these organosilanes which are preferably used are the bis-(trialkoxysilyl-alkyl)-oligosulphides, such as bis-(trimethoxy-,-(triethoxy-,-(trimethoxyethoxy-,-(tri-n-propoxy-,-(tributoxy-,-(tri-i-propoxy and-(tri-i-butoxy silyl methyl)-oligosulphides and the corresponding -silylethyl)- 40 40 oligosulphides, that is to say the di-, tri-, tetra-, pentahexa-, hepta- and octa-sulphides, respectively, also the bis-(3-trimethoxy-, -(triethoxy-, tri-(methoxyethoxy-,-(tripropoxy-,-(tri-n-butoxy-and-(tri-i-butoxysilyl propyl)-oligosulphides, i.e. once again the di-, tri-, tetra- and so on up to the octa-sulphides, the corresponding bis-(3-trialkoxo silyl isobutyl)-oligosulphides, the corresponding bis-(4-trialkoxo 45 45 silylbutyl)-oligosulphides and so on up to the bis-(10-trialkoxo silyl decyl)-oligosulphides. Of these selected, relatively simple trialkoxy silanes of general formula II and their mixtures, it is preferred to use the bis-(3-trimethoxy-,-(triethoxy- and-tripropoxy-silyl-propyl)-polysulphides, namely the di-, tri- and tetra-sulphides, the triethoxy compounds containing 2, 3 or 4 sulphur atoms and mixtures thereof being particularly preferred. These oligosulphidic silanes are preferably used in quantities of from 1 to 15 parts 50 50 by weight per 100 parts by weight of silicate filler in the new rubber mixtures preferably vulcanisable with sulphur.

The above-mentioned oligosulphidic alkoxy or phenoxy silyl compounds may be replaced by their completely or partly hydrolysed compounds. Alternatively, these completely or partly hydrolysed compounds may replace part of the non-hydrolysed compounds.

55 The following mercapto silanes corresponding to formula III are preferably used: mercapto methyl trimethoxy silane, mercaptomethyltriethoxysilane, mercaptomethyltri-i-propoxysilane, 2- 55 mercaptoethyltrimethoxysilane, 2-mercaptoethyltriethoxysilane, 2-mercaptoethyltri-i-propoxysilane, 2-mercaptoethyltributoxysilane, 2-mercaptoethyltri-n-propoxysilane, 2-mercaptoethyldiethoxymethylsilane, 2-mercapto-2-methylethyltriethoxysilane, 2-mercapto-1- 60 60 methylethyltrimethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropyltriethoxysilane, 3-mercaptopropyltri-i-propoxysilane, 3-mercaptopropyltri-n-propoxysilane, 3-mercaptopropyltributoxysilane, 3-mercaptopropyltris-(methoxyethoxy)-silane, 4-mercaptobutyltriethoxysilane, 5-mercaptopentyltrimethoxysilane, 5-mercaptopentyltri-i-propoxysilane,

3-mercaptopropyldiethoxyethylsilane, 3-mercaptopropyldipropoxypropylsilane, 6-mercaptopohexyltriethoxysilane, 8-mercaptopoctyltrimethoxysilane and 10-mercaptodecyltriethoxysilane.

The present invention also provides a process for vulcanising a rubber mixture by heating the mixture after forming to temperatures from 100 to 250°C for a period of time, dependant on the heating temperature, of from 1 to 200 minutes, the rubber mixture comprising at least one vulcanisable halogen-free rubber or a mixture of one or more halogen-free rubbers with at most 80% based on the total weight of the rubber, of at least one halogen-containing rubber; at least one silicate filler in quantities of from 1 to 250 parts by weight; at least one oxide of the metals zinc, magnesium and lead in quantities of from 0 to 15 parts by weight, at least one monobasic fatty acid containing from 12 to 24 carbon atoms in the alkyl chain, benzoic acid or salicylic acid in quantities of from 0 to 10 parts by weight; optionally sulphur and/or sulphur donors in quantities of from 0.1 to 15 parts by weight, at least one vulcanisation accelerator in quantities of from 0.1 to 10 parts by weight; at least one plasticiser in quantities of from 0 to 100 parts by weight; at least one stabiliser from the group comprising anti-agers, anti-fatigue agents, oxidation inhibitors, light stabilisers and anti-oxonants in respective quantities of from 0 to 10 parts by weight; carbon black in quantities of from 0 to 150 parts by weight; optionally other standard rubber auxiliaries in the usual quantities and having uniformly distributed therein from 0.1 to 20 parts by weight of at least one organosilane corresponding to the following general formula



in which X represents chlorine or bromine, p is 1 or 2, m is 1 to 5, R¹ represents a C₁—C₅-alkyl group, a C₅—C₈-cycloalkyl group or a phenyl group, R represents a C₁—C₅-alkyl group, a C₅—C₈-cycloalkyl group, a methoxyethyl group, a phenyl group or a benzyl group and n is 0, 1 or 2, or a hydrolysate and/or a condensate thereof, all the quantities specified being based on 100 parts by weight of the rubber.

Thus the rubber mixtures are as described above and they are prepared in the usual way. A two-stage mixing cycle is preferred. In the first stage, the following constituents are mixed in a kneader at a throughflow temperature in the range from 55 to 85°C and preferably at a throughflow temperature of 60°C:

in the first minute, the rubber and—where a halogenated rubber is additionally present—also a metal oxide, for example magnesium oxide;
in the following one and a half minutes, half the silicate filler, zinc oxide, stearic acid and silane(s);
in the following one and a half minutes, the second half of the silicate filler and the plasticiser (for example plasticiser oil), if any, and the remaining constituents of the mixture, except for the sulphur and the accelerator; after a total of four and a half minutes, the mixture is removed from the kneader and stored for 24 hours at room temperature.

In the second stage of the mixing cycle, the sulphur and the accelerator(s) are added to and mixed with the master batch from the first stage on a pair of rolls or in a kneader over a period of 1.5 minutes at a starting temperature of the order of 80°C.

This two-stage mixing process avoids premature prevulcanisation of the mixture.

The trend followed by the vulcanisation of a rubber mixture may be represented for example by a vulcameter curve. The vulcameter curve is formed for example by plotting the torques determined by means of a vulcameter (see DIN 53 529) on the abscissa of a rectangular co-ordinate system against the vulcanisation time on the ordinate. The onset of vulcanisation is reflected in a climbing branch of the vulcameter curve. The curve then normally reaches a maximum or indicates a maximum value and then falls more or less quickly or slowly in most cases as vulcanisation continues. Vulcameter curves recorded at a constant temperature are also known as crosslinking isotherms.

In the vulcanisation of rubber mixtures based on natural or synthetic rubbers in the presence or absence of rubber fillers by means of sulphur and vulcanisation accelerators, as normally practised in industry, the crosslinking isotherms mentioned above usually pass through a maximum which is formed in consequence of the fact that, during the complex chemical processes involved, the build up of polysulphidic crosslinking sites between the rubber molecules predominates in the initial stage of vulcanisation, whereas the degradation of intermolecular polysulphidic and disulphidic bridge bonds into intramolecular heterocyclic rings takes place in the final stage. In a vulcametric crosslinking isotherm, these phenomena are distinguished by a continuous fall in the crosslinking isotherm, i.e. in a reduction in the torque values, and in practice by moduli which decrease with increasing vulcanisation time. The change in the relative crosslink density of the vulcanisate (level of the torques) and the relative crosslink density present at any time during the vulcanisation process may be read off from the trend of the vulcametric crosslinking isotherm. The change in the crosslink densities is accompanied by a change in the mechanical properties of the vulcanisates, providing this property is dependent upon the crosslink density, such as tensile strength, breaking elongation, elasticity, Shore hardness, heat built-up, wear, etc. In practice, the downwardly sloping branch of the vulcameter curve represents a deterioration in the above-mentioned properties of the vulcanisate. This phenomenon is known among experts as "reversion".

The rubber mixtures according to the invention are particularly suitable for the production of motor vehicle tyres, e.g. car tyres, lorry tyres and tyres for cross-country vehicles, for the production of treads

for motor vehicle tyres and for the production of industrial rubber products and shoe soles.

Thus, industrial applications for the rubber mixtures according to the invention and their vulcanisates are, for example, industrial rubber products, such as cable sheaths, hoses, heating hoses, also electrical insulations, linings, impregnations and coatings of heat-resistant fabrics, particularly drive belts, V-belts, conveyor belts, roll coverings, seals, and also shoe soles, damping and vibration elements and similar articles which have to satisfy stringent requirements in regard to elasticity properties, as determined in particular by the compression set test (DIN 53 517), and also in regard to temperature and/or oil resistance.

The outstanding effect of the halogen silanes corresponding to general formula (I) in mixtures or moulding compositions containing halogen-free rubber and their crosslinking products or vulcanisates was extremely surprising.

Without limiting the invention in any way, some formulations for the new rubber mixtures of the vulcanisates or crosslinking products are given by way of example in the following with evaluations and comparisons of the results. Since many different expressions repeatedly occur, the following abbreviations have been used.

List of Abbreviations used

<u>Abbreviation</u>	<u>Meaning</u>	<u>Measured in</u>	
t_5	Mooney Scorch time (130°C)	minutes	
t_{35}	Mooney cure time (130°C)	minutes	
ML 4	Mooney plasticity or viscosity (determined at 100°C using the normal rotor (L) test time: 4 minutes)	Mooney units (torque)	20
MS 4	ditto using the small rotor (S)	Mooney units	
ZF	tensile strength	kp/cm ²	
M 200	modulus at 200% elongation	kp/cm ²	25
M300	modulus at 300% elongation	kp/cm ²	
VW	tear propagation resistance (at°C)	kp/cm	
BD	breaking elongation	%	
SH	Shore-A-hardness	—	30
A	wear (also "DIN-wear")	mm ³	
CS	compression set B, 22 hours, 70°C	%	
D_{min}	minimum torque (Rheometer test)	mkp	
D_{max}	maximum torque	mkp	
$D_{120'}$	torque after 120 minutes' Rheometer testing	mkp	35
$D_{60'}$	torque after 60 minutes' Rheometer testing	mkp	
$t_{10\%}$	reaction time up to 10% conversion	minutes	
$t_{80\%}$	reaction time up to 80% conversion	minutes	40
$t_{95\%}$	reaction time up to 95% conversion of the vulcanisation reaction, based on the maximum conversion (same vulkometer curve) and so on, including differences therein	minutes	45

Test Standards

The physical tests were carried out at room temperature in accordance with the following Standards:

5	Tensile strength, breaking elongation and modulus using 6 mm thick rings	DIN 53 504	5
	Tear propagation resistance	DIN 53 507	
	Shore-A-hardness	DIN 53 505	
10	Mooney test	DIN 53 523 and DIN 53 524 or ASTM D 927—57 T	10
	Wear, also called DIN-wear	DIN 53 516	
15	Compression set	DIN 53 517 ASTM D 395	15
	Rheometer test/vulcanometry	DIN 53 529 (Provisional October 1972)	

20 The vulcanisates or test specimens were produced in a steam-heated multistage press using the vulcanisation temperatures and heating times indicated. 20

In the Examples, the quantities in which the mixture components are used are given in parts by weight.

The respective comparison mixtures are identified by the letter "V" before the number. The corresponding mixtures according to the invention are identified by the letter "E".

25 The mixtures were prepared in two separate phases in a standard kneader which had been heated to an initial temperature of 80°C and of which the rotor had been set at 40 revolutions per minute (r.p.m.). Friction amounted to 1:1.16. 25

30 In the first mixing phase, the total quantity of rubber was introduced over a period of 1 minute, after which the first half of the filler, the zinc oxide, the stearic acid and the silane were added over a period of about 1.5 minutes. The second half of the filler was then added, again over a mixing period of 1.5 minutes. The subsequent general cleaning of the kneader elements, such as for example the plunger, took half a minute and, after a total mixing time of 5 minutes, the master batch formed was removed from the kneader. 30

35 The master batch was then stored for 24 hours at room temperature. The second mixing phase was then carried out using the same kneader, the same rotational speed, friction and initial temperature, the master batch, the sulphur and the accelerator(s) being added over a period of 1.5 minutes and all the components being processed to form a mixture characterised by uniform distribution of its various components. 35

40 As the results of the measurements on the rubber mixtures and the vulcanisates show, the described mixing process is the most favourable in overall terms. In this process, the components zinc oxide and stearic acid are added towards the beginning of mixing. 40

In Example 1 below, the mixture thus formed are denoted V 1.1 (comparison mixture of Example 1 No. 1), E 1.1.1 (mixture according to the invention of Example 1 No. 1.1) and E 1.2.1 (mixture according to the invention of Example 1 No. 2.1).

45 If, by contrast, the zinc oxide or analogous metal oxides and the stearic acid or analogous organic acids, particularly analogous fatty acids, are added and worked in later in the mixing process, for example, in the second phase, distinct differences become visible in the properties of the mixtures and the vulcanisates, for example in the Mooney viscosities and plasticities, and also in the properties of the vulcanisates. The Mooney viscosities MS 4 of corresponding alternative mixtures were also measured. 45

50 The mixtures in question are comparison mixture V 1.2 and the mixtures according to the invention E 1.1.2 and E 1.2.2. 50

Mooney plasticity (MS 4-values) were determined in accordance with DIN 53 523 using the small rotor at a test temperature of 100°C (see Table I below).

EXAMPLES

55 1) Three rubber mixtures are prepared from the following ingredients: 55

Mixtures	V 1.1 and V 1.2	E.1.1.1 E.1.1.2	E 1.2.1 E 1.2.2		
5	Styrene-butadiene rubber (SBR 1500)	100	100	100	5
	Granulated, active precipitated silica filler ¹⁾ (Degussa's Ultrasil VN 3)	50	50	50	
	Active, finely divided zinc oxide	4	4	4	
10	Mixtures	V 1.1 V 1.2	E.1.1.1 E.1.1.2	E.1.2.1 E.1.2.2	10
	Stearic acid	2	2	2	
	Chloropropyl triethoxy silane	—	3	7.5	
	N-cyclohexyl-2-benzothiazole sulphenamide	1	1	1	
15	Sulphur	2	2	2	15

The mixtures thus formed are denoted V 1.1 (comparison mixture of Example 1 No. 1), E.1.1.1 (mixture according to the invention of Example 1 No. 1.1) and E 1.2.1 (mixture according to the invention of Example 1 No. 2.1).

1) Mean primary particle size of this filler 18 μm and specific surface (DIN 66 132) 175 m^2/g .

20	Mixture	V 1.1	E.1.1.1	E.1.2.1	V.1.2	E.1.1.2	E.1.2.2	
	MS 4	82	78	70	140	108	76	20
	D_{\min}	0.121	0.116	0.098	0.275	0.141	0.110	
	$D_{120'}$	0.757	0.840	1.083	0.977	0.897	1.091	
	$D_{120'} - D_{\min}$	0.636	0.724	0.985	0.702	0.755	0.981	
25	t 10%	11.7	14.7	12.0	17.2	16.1	17.2	25
	t 90%	60.4	80.5	64.4	84.4	76.3	62.6	
	t 95%	71.0	93.1	86.1	95.0	89.4	74.8	
	t 90%—t 10%	48.7	65.8	52.4	67.2	60.1	45.4	
	$D_{120'} - D_{60'}$	9.4	20.2	11.2	25.4	17.7	9.8	
30	$D_{120'} - D_{\min}$							30
	ZF	14.0	21.6	20.0	12.9	17.3	16.5	
	M 300	3.0	4.3	8.9	3.0	4.1	8.4	
	BD	710	700	470	720	660	440	
	E	34	35	37	37	34	36	
35	SH	59	61	68	61	59	66	35
	A	170	124	91	169	125	87	

In Table I and also in the following text, the D-values represent the torques as determined by

means of a vulcameter or rheometer in meterkiloponds (mkp). The torque are taken from vulcammetric crosslinking isotherms. An MPV rheometer of the type manufactured by Monsanto Europe S.A. B—1150 Brussels, was used as the vulcameter. Rheometer testing was carried out under the following conditions: deformation amplitude 3°C, test frequency 3 cycles per minute, test temperature 160°C and running time 2 hours. So far as the expressions vulcammetry and crosslinking isotherms are concerned, reference is made to the Provisional Standard DIN 53 529 of February 1971, particularly page 1.

The figures in Table I show that the silanes bring about a distinct reduction in the viscosities of the rubber mixtures according to the invention, which is equivalent to a reduction in the energy expended. The reduction in viscosity becomes even clearer or more advantageous if, as shown, the silane content of the mixtures is increased. In that case, the viscosity may be correspondingly reduced further than shown and vice versa.

2) Silanes of the type indicates were worked in the quantity indicated into a basic mixture of:

	<u>Constituents</u>	<u>Parts by Weight</u>	
15.	Natural rubber (SMR 5; ML 4 = 67)	100	15.
	Silica filler (as in Example 1)	50	
	Zinc oxide	4	
	Stearic acid	2	
	Silane; various	as indicated below	
20	N-cyclohexyl-2-benzothiazole sulphenamide	1.5	20
	Sulphur	2	

A comparison mixture contained no silane whilst another mixture contained 6 parts by weight of the technical silane Si 69 consisting essentially of bis-(3-triethoxysilylpropyl)-oligosulphide having a minimum sulphur content of 22.0% by weight according to the prior art. Two mixtures according to the invention contained 6 parts by weight of 3-chloropropyl triethoxy silane (CI-PTES in short) and 8 parts by weight of CI-PTES.

The four mixtures were prepared as described above. Part of the rough sheet formed was moulded to form 6 mm thick plates measuring 20 x 10 cm which were vulcanised at 150°C. Another part of the four mixtures was rheometer-tested at 150°C. The following results were obtained.

TABLE II

	Without silane	With Si 69 6 parts by wt.	with CI-PTES	
			6 parts by wt.	8 parts by wt.
D _{min}	3.36	0.77	0.65	0.58
ML 4	161	75	72	66
t 10%	20	15.3	29.4	31
t 80%—t20%	120	6.4	6.1	4.2
WW	7	39	42	47
SH	62	63	57	58
CS (22 hours; 70°C, non-aged)	32.7	17.7	16.9	17.8

3) The same silane corresponding to the prior art (Si 69) and, according to the invention, CI-PTES were again worked in the same quantities into the same basic mixtures as in Example 2, except for 100

parts by weight of polyisoprene rubber (Natsyn 2200, a product of Goodyear Tire Rubber Co., Chem. Div., Akron 16, Ohio, USA) instead of the natural rubber. A mixture with no silane added was also tested for comparison. The following results were obtained (tests carried out in the same way as in Example 2).

TABLE III

	Without silane	With Si 69 6 parts by wt.	with CI-PTES	
			6 parts by wt.	8 parts by wt.
D _{min.}	4.18	1.30	1.00	0.85
ML 4	136	87	77	71
t 10%	8.5	15.7	36	39
t 80%—t 20%	15.1	5.4	6.3	4.6
WW	9	33	33	39
SH	66	66	54	59
CS	28.2	14.5	12.8	12.8
(22 hours; 70°C, non-aged)				

5 Table III reveals in particular distinct improvements in the viscosities of the mixture and in the tear propagation resistance and compression set values. 5

4) Rubber mixtures were prepared from the following constituents and tested in the same way as in the preceding Examples.

	<u>Constituents</u>	<u>Parts by weight</u>	
10	Polybutadiene rubber (98% cis-1,4-content)	70	10
	Natural rubber (First Latex Crepe)	30	
	Silica filler (see Example 1)	50	
	Zinc oxide (red seal quality)	4	
	Stearic acid	2	
15	Naphthenic plasticiser oil (cold setting point — 28°C)	12	15
	Anit-ager, a mixture of aralkylated phenols (D = 1.06 g/ml; Bp _{0,4} = 130°C)	1	
	Silanes, various	as indicated below	
20	Accelerator zinc ethyl phenyl dithiocarbamate	0.5	20
	Benzothiazole-2-dicyclohexyl	1	
	Sulphur	1.67	

A comparison mixture was prepared without any of addition of silane and another comparison mixture contained 3.3 parts by weight of the silane Si 69 (see Example 2). The mixtures according to the invention contained 6 and 8 parts by weight of the silane CI-PTES (see Example 2).

25

TABLE IV

	Without silane	With Si 69 3.3 parts by wt.	with CI-PTES	
			2 parts by wt.	4 parts by wt.
D _{min}	3.18	1.32	1.79	1.14
ML 4	148	51	62	58
t 10%	—	8.8	12.8	13.4
t 80%—t 20%	120	3.4	5.4	3.1
WW	23	17	18	26
SH	62	58	47	50

5) Rubber mixtures were prepared as described above from the following constituents and tested in the same way as in the preceding Examples.

	<u>Constituents</u>	<u>Parts by weight</u>	
5	Styrene-butadiene rubber (SBR 1712)	96.2	5
	cis-1,4-polybutadiene rubber (see Example 4)	30	
	Precipitated, active granulated silica filler (mean primary particle size 28 μm , specific surface (DIN 66 132) 130 m^2/g)	30	
10	Rubber-grade carbon black N 339	40	10
	Zinc oxide (see Example 4)	4	
	Stearic acid	2	
	N-isopropyl-N'-phenyl-p-phenylene diamine	2	
	Poly-2,2,4-trimethyl-1,2-dihydroquinoline	1	
15	Anti-ozonant wax (paraffin-based, solidification point 61—65°C, type G 35)	1	15
	Plasticiser oil, highly aromatic, cold setting point $\pm 0^\circ\text{C}$	20	
20	Polyethylene glycol (average molecular weight 4000)	1	20
	Silanes, various	quantities as indicated below	
	Tetramethyl thiuram monosulphide	0.3	
	N-tert.-butyl-2-benzothiazyl-sulphenamide	1	
25	Sulphur	2.2	25

A comparison mixture prepared therefrom did not contain any silane, another mixture contained 3.6 parts by weight of the technical silane Si 69 (see Example 2) and the two mixtures according to the invention contained 3.6 parts by weight and 4.8 parts by weight of CI-PTES (see Example 2).

TABLE V

	Without Silane	With Si 69 3.6 parts by weight.	With CI-PTES	
			3.6 parts by wt.	4.8 by wt.
D _{min}	0.74	0.71	0.65	0.67
ML 4	51	50	46	46
t 10%	11.5	9.8	12.3	12.0
t 80%—t 20%	2.1	2.0	1.9	1.7
WW	20	18	24	24
SH	54	58	53	53
CS	21.2	20.7	20.2	19.3
(22 hours; 70°C, non-aged)				

6) Four mixtures based on butyl rubber were prepared from the following constituents and tested in the same way as described above.

	<u>Constituents</u>	<u>Quantities in parts by weight</u>	
5	Isoprene-isobutylene rubber	100	5
	Active, granulated silica filler (see Example 1)	50	
	Zinc oxide (see Example 4)	5	
	Stearic acid	1	
	Naphthenic plasticiser oil (see Example 4)	5	
10	Polyethylene glycol (see Example 5)	3	10
	Silanes, various	quantities as indicated below	
	Tetramethyl thiuram disulphide	2	
	Dipentamethylene thiuram tetrasulphide	1	
15	Sulphur	1.7	15

A first comparison mixture was prepared without any silane, a second was prepared with 6 parts by weight of the silane Si 69 (see Example 2) and two mixtures according to the invention were prepared with 6 parts by weight and 8 parts by weight of the silane CI-PTES. The test results obtained were as follows.

TABLE VI

	Without silane	With Si 69 6 parts by wt.	with CI-PTES	
			6 parts by wt.	8 parts by wt.
D _{min.}	2.16	0.72	0.75	0.64
MI 4	112	67	68	62
t 10%	6.1	6.8	6.2	6.2
t 80%—t 20%	17	11.7	6.0	7.6
WW	13	7	16	—
SH	64	69	61	62
CS	34.1	29.2	27.8	27.2
(22 hours; 70°C, non-aged)				

7) The following four mixtures based on butadieneacrylonitrile rubber were prepared and tested in the same way as in the preceding Examples.

	<u>Constituents</u>	<u>Quantities</u>	
5	Butadiene-acrylonitrile rubber with an acrylonitrile content of 34% and a Mooney viscosity of 45	100	5
	Active, granulated silica filler (see Example 5)	50	
	Zinc oxide (see Example 2)	5	
	Stearic acid	1	
10	Diocyl phthalate	15	10
	Silanes, various	quantities as indicated below	
	Tetramethylthiuram disulphide	2.5	
	N-cyclohexyl-2-benzothiazole sulphenamide	1.5	

15 The two comparison mixtures were again prepared on the one hand without any silane and, on the other hand, with 6 parts by weight of the known silane Si 69, whilst the two mixtures according to the invention were prepared with 6 parts by weight and 8 parts by weight of the silane CI-PTES. A few selected, representative test results are set out in the following Table:

TABLE VII

	Without silane	With Si 69 6 parts by wt.	with CI-PTES	
			6 parts by wt.	8 parts by wt.
D _{min}	1.32	0.68	0.74	0.53
ML 4	84	56	59	51
WW	26	7	20	20
SH	61	55	53	68

8) The following four mixtures based on styrene-butadiene rubber were prepared and tested in the same way as in the preceding Examples.

	<u>Constituents</u>	<u>Quantities</u>	
5	EPDM-rubber (Buna AP 541, a product of Buna-Werke Huls GmbH, 4370 Marl)	100	5
	Active, granulated silica filler (see Example 5)	50	
	Zinc oxide (see Example 2)	3	
	Stearic acid	1	
10	Plasticiser oil, paraffinic (Manufacturer: Sun Oil Corp., Texas, U.S.A.)	50	10
	2,6-di-tert.-butyl-4-methyl phenol	1	
	Silanes, various	quantities as indicated below	
	Di-2-benzothiazyl disulphide	1.5	
15	Morpholine disulphide	1.5	15
	Tetramethyl thiuram disulphide	2.5	

A first comparison mixture was prepared without any silane, a second comparison mixture was prepared with 6 parts by weight of the silane Si 69 and two mixtures according to the invention were prepared with 6 parts by weight and 8 parts by weight of CI-PTES (Silane). A few selected representative test results are set out in the following Table.

TABLE VIII

	Without silane	With Si 69 6 parts by wt.	With CI-PTES	
			6 parts by wt.	8 parts by wt.
D _{min.}	1.04	0.57	0.56	0.51
ML 4	76	58	52	48
t 10%	4	4.9	5.1	5.2
t 80%—t 20%	2.7	4.1	2.8	2.8
ZF	9.8	9.7	11.8	11.9
WW	11	6	8	8
SH	53	56	51	50
CS	26.9	10.7	9.9	10.4
(22 hours; 70°C, non-aged)				

These results show *inter alia* improvements in the viscosities of the mixtures and in the tensile strength, tear propagation resistance and Shore hardness values.

9) Four mixtures based on styrene-butadiene rubber were prepared from the following constituents and tested in the same way as in the preceding Examples.

	<u>Constituents</u>	<u>Quantities</u>	
	Styrene-butadiene rubber (SBR 1500)	100	
	Clay (Suprex Clay, a product of the J. M. Huber Corp., Locust, N.J., U.S.A.)	80	
5	Zinc oxide (see Example 2)	4	5
	Stearic acid	2	
	Silanes, various	Quantities as shown below	
	N-cyclohexyl-2-benzthiazole sulphenamide	1.5	
10	Sulphur	2	10

A first comparison mixture was prepared without any silane, a second comparison mixture was prepared with 3 parts by weight of the technical silane Si 69 and two mixtures according to the invention were prepared with 4 parts by weight and 8 parts by weight of the silane CI-PTES. The mixtures were tested in the same way as in the preceding Examples and produced the following results:

TABLE IX

	Without silane	With Si 69 3 parts by wt.	with CI-PTES	
			4 parts by wt.	8 parts by wt.
D _{min.}	0.88	0.94	0.79	0.77
ML 4	75	79	69	67
WW	12	13	12	15

10) Oil-extended polybutadiene rubber is also accessible to the invention, as shown by the following mixtures of the constituents indicated. The corresponding test results are shown in Table X.

	<u>Constituents</u>	<u>Quantities</u>	
20	Polybutadiene rubber oil-extended with 37.5 parts by weight of oil to 100 parts by weight of rubber	137.5	20
	Active, granulated silica filler (see Example 1)	50	
	Zinc oxide (see Example 2)	4	
	Stearic acid	2	
25	Silanes, various	quantities as shown below	25
	N-tert.-butyl-2-benzothiazole sulphenamide	1.5	
	Sulphur	2	

TABLE X

	Without silane	With Si 69 6 parts by wt.	With CI-PTES	
			6	8 parts by wt.
D _{min.}	2.48	1.14	1.16	1.01
SH	53	52	40	42

11) Where other silanes according to the invention are used, mixtures of the following constituents show that valuable effects are again obtained.

	<u>Constituents</u>	<u>Quantities</u>	
5	Styrene-butadiene rubber (SBR 1500)	100	5
	Active, granulated silica filler (see Example 1)	50	
	Zinc oxide (see Example 2)	4	
	Stearic acid	2	
10	Silanes, various	quantities as shown below	10
	N-cyclohexyl-2-benzothiazole sulphenamide	1.5	
	Sulphur	2	

15 A comparison mixture was prepared without any silane. The mixtures according to the invention contained four different silanes (see Table XI, *inter alia* silanes A, B and C) in equimolar quantities. The tests were carried out in the same way as in the preceding Examples. A few representative results are set out in the following Table. 15

TABLE XI

	Without silane	CI-PTES 7.5	Silane A 6.2	Silane B 7.6	Silane C 7.9 parts by wt.
D _{120'} -D _{min}	6.9	11.2	10.8	12.9	8.0
ZF	15.8	19.7	20.0	20.7	18.3
M300	3.4	8.8	8.9	15.3	4.6
BD	740	420	470	360	660
SH	62	67	69	73	64
A	172	103	97	75	163

Silane A = chloropropyl trimethoxy silane

Silane B = bromopropyl trimethoxy silane

Silane C = chlorobutyl triethoxy silane

20 This Examples illustrates above all the surprising fact that the use of halogenalkyl alkoxy silanes eliminates the otherwise frequent need to add so-called secondary accelerators, such as glycols and amino compounds. Compared with a comparison mixture, a so-called zero mixture, there is a considerable increase in the tensile strength and modulus 300 (modulus at 300% elongation) values. 20

The Shore hardness and breaking elongation values follow the modulus values. Surprisingly, wear is also considerably improved.

In general, the CI-PTES produces a surprisingly sharp reduction in the viscosities of the mixtures as reflected in the D_{\min} -values (150°C) and in the ML 4- and MS 4-values. Depending on the type of rubber or rubber blend, this valuable effect is more or less more pronounced than can be obtained by adding the known silane Si 69. 5

12) The following mixtures based on styrene-butadiene rubber (SBR 1502) are practical mixtures for the production of transparent shoe soles.

	<u>Constituents</u>	<u>Quantities</u>	
10	SBR 1502	100	10
	Zinc oxide (see Example 2)	3	
	Stearic acid	1	
	Mixture of aralkylated phenols (see Example 4)	1	
	Salicylic acid	0.8	
15	Active granulated silica filler (see Example 1)	50	15
	Silane	quantities as shown below	
	Zinc-2-mercaptobenzthiazole	1.75	
	Diphenyl guanidine	1.75	
20	Hexamethylene tetramine, granulated (containing 3% by weight of silica filler)	1	20
	Sulphur	2	

A comparison mixture contained no added silane. The mixtures according to the invention contained 5 parts by weight and 7.5 parts by weight of CI-PTES (see Example 2). This silane was advantageously added immediately after introduction of the rubber into the mixer together with the first half of the silica filler. The temperature at the beginning of the first mixing phase was 80°C. At the beginning of the second mixing phase (after intermediate storage for 24 hours), it was 50°C. In other respects, the mixtures were prepared and tested in the same way as described above (rheometer test at 150°C). 25

TABLE XII

	Without silane	5	with CI-PTES 7.5 parts by wt.
D_{\min}	1.26	1.21	1.14
D_{\max}	11.75	13.12	13.47
$D_{\max} - D_{\min}$	10.49	11.91	12.33
t 95%	11.7	16.0	27.9
t 90% - t 10%	5.1	8.6	14.1
$\frac{D_{\max} - D_{(\max+60')^1}}{D_{\max}}$	5.1	1.9	0.3
ML 4	104	101	97
t 5	3.1	2.8	1.6
t 35	4.0	3.7	2.4
ZF	10.2	12.7	-
M300	4.4	6.5	7.7
SH	62	69	70
A	114	108	110

¹⁾ The value of this fraction is called reversion and is measured in percent.

The above test results show emphatically that the addition of silane leads to falling viscosities, to a reduced vulcanisation rate and to lower reversion. 0.3% signifies a substantially reversion-free mixture or rather a reversion free vulcanisate. It is added by way of explanation that the value $D_{(\max+60')}$ is that torque which is measured at the time 60 minutes after appearance of the maximum torque. The vulcanisates show distinct increases in moduli, Shore hardness and wear.

13) The following mixtures contain a mixture of two different rubbers, namely a halogen-free rubber and a halogen-containing rubber.

	<u>Constituents</u>	<u>Quantities</u>	
10	Styrene-butadiene rubber (SBR 1500)	60	10
	Polychlorobutadiene rubber (chlorine content approximately 38%; viscosity 40 to 45 Mooney units: Baypren 210, a product of Bayer AG)	40	
	Silica filler (see Example 1)	50	
15	Magnesium oxide	2	15
	Stearic acid	2	
	Silane	as shown below	
	Zinc oxide (see Examples 1 and 4)	5	
	N-cyclohexyl-2-benzothiazole sulphenamide	1	
20	Sulphur	2	20

The mixture according to the invention (E 13) contained as silane 7.5 parts by weight of purified distilled CI-PTES. The comparison mixture (V13) was a so-called zero mixture. The mixtures were prepared and tested in the same way as in the preceding Examples.

TABLE XIII

Test	Mixture	
	V13	E13
ML 4 (100°C)	155	121
D _{min}	2.86	1.64
ZF	10.9	16.1
M200	3.7	5.6
M300	6.0	9.8
A	171	116
CS (22h; 70°C; non-aged)	12.1	8.6

- 5 The addition of chloropropyl triethoxy silane greatly reduces the Mooney viscosity which leads to better processibility coupled with an improvement in the static properties of the vulcanisate: higher tensile strength, higher moduli, higher resistance to wear and lower (better) compression sets. The advantages of the mixture according to the invention containing the comparatively simple chlorosilane, i.e. comparatively simple in structure and to prepare, and the vulcanisate obtained therefrom are obvious.
- 10 14) The following mixtures based on styrene-butadiene rubber (SBR 1500) demonstrate the advantageous use of master batches of silane and filler with synergistic effects.

Constituents	Mixture No. (quantities in parts by weight)						
	V14.1	E14.1	V14.2	E14.2	E14.3	E14.4	
15 SBR 1500	100	100	100	100	100	100	15
Zinc oxide (see Example 1)	4	4	4	4	4	4	
Stearic acid	2	2	2	2	2	2	
Silica filler (see Example 1)	50	50	50	50	50	42.5	
HAF-carbon black N330	—	—	7.5	7.5	—	—	
20 CI-PTES purified with ammonia	—	7.5	—	7.5	—	—	20
Carbon black/CI-PTES master batch ¹⁾	—	—	—	—	15	—	
Silica filler/CI-PTES master batch ²⁾	—	—	—	—	—	15	
25 N-cyclohexyl-2-benzothiazole sulphenamido	1.5	1.5	1.5	1.5	1.5	1.5	25
Sulphur	2	2	2	2	2	2	

¹⁾ 1:1-mixture of HAF-carbon black, powder form (BET-surface 78 m²/g; mean primary particle size 27 nm) and CI-PTES

30 ²⁾ 1:1-mixture of silica filler (according to Example 1) and CI-PTES

The six mixtures, of which four correspond to the invention (E14.1 to E14.4), were prepared and tested in the same way as in the preceding Examples. The relevant test results are set out in the following Table (vulcanisation temperature = 160°C).

TABLE XIV

	V14.1	E14.1	V14.2	E14.2	E14.3	E14.4
Vulcanisation Time	85	80	80	80	80	80
ZF	16.2	18.7	18.5	16.2	17.7	17.7
M200	2.5	5.9	3.5	5.1	6.1	7.0
M300	4.5	11.3	6.2	10.4	12.2	13.9
BD	620	390	550	340	370	340
SH	62	69	70	72	72	69
A	133	91	118	93	91	91
Rheometer test						
D_{\min}	1.90	1.36	2.37	1.42	1.52	1.58
$D_{120'}$	8.49	12.53	10.07	13.47	13.88	12.38
$D_{120'} - D_{\min}$	6.58	11.18	7.70	12.05	12.36	10.80
$D_{120'} - D_{60'}$	16.5	8.2	11.1	6.5	7.7	10.3
$D_{120'} - D_{\min}$						
Mooney Test						
ML4 (100°C)	155	122	172	124	127	132
t_5 (130°C)	>70	83.7	60.0	61.7	64.1	85.4

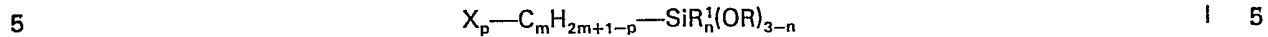
5 The figures representing the test results show the following. The addition of 7.5 parts by weight of 5
3-chloropropyl triethoxy silane to the comparison or zero mixture V14.1 produces the following
improvement: increase in tensile strength, drastic increase in moduli and Shore hardness and
improvement in wear (E14.1). As expected, the addition of carbon black produces smaller
improvements in the properties of the vulcanisates and also a slight improvement in the rheometer
10 values, whereas Mooney viscosity—again as expected—is adversely affected (V14.2 compared with 10
V14.1). If now the silane is added (see E14.2 compared with V14.2), the desired, in some cases very
distinct improvements according to the invention are again obtained, the sole exception being tensile
strength.

15 However, if the master batches are used instead of the separate individual additions, further 15
improvements are surprisingly obtained in the moduli and cross-link density both in the case of the
black mixture and in the case of the white mixture. These synergistic effects were confirmed after the
master batches had been stored for 2 months which is attributable to high stability in storage of the
master batches.

CLAIMS

20 1. A vulcanisable rubber mixture of at least one vulcanisable halogen-free rubber or of a mixture of 20
one or more halogen-free rubbers with at most 80%, based on the total weight of the rubber, of at least
one halogen-containing rubber; at least one silicate filler in quantities of from 1 to 250 parts by weight,
at least one oxide of the metals zinc, magnesium and lead in quantities of from 0 to 15 parts by weight;
at least one monobasic fatty acid containing from 12 to 24 carbon atoms in the alkyl chain, benzoic acid
25 or salicylic acid in quantities of from 0 to 10 parts by weight; optionally sulphur and/or sulphur donors in 25
quantities of from 0.1 to 15 parts by weight; at least one vulcanisation accelerator in quantities of from
0.1 to 10 parts by weight; at least one plasticiser in quantities of from 0 to 100 parts by weight; at least
one stabiliser from the group comprising anti-agers, anti-fatigue agents, oxidation inhibitors, light

stabilisers and anti-ozonants in respective quantities of from 0 to 10 parts by weight; carbon black in quantities of from 0 to 150 parts by weight; and at least one organosilane, the rubber mixture containing as organosilane from 0.1 to 20 parts by weight of at least one compound corresponding to the general formula

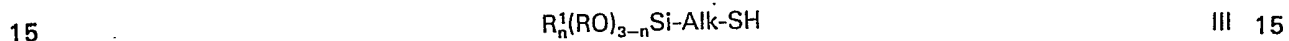


in which X represents chlorine or bromine, p is 1 or 2, m is 1 to 5, R¹ represents a C₁—C₅-alkyl group, a C₅—C₈-cycloalkyl group or a phenyl group, R represents a C₁—C₅-alkyl group, a C₅—C₈-cycloalkyl group, a methoxyethyl group, a phenyl group or a benzyl group and n is 0, 1 or 2, or a hydrolysate and/or a condensate thereof, all the quantities specified being based on 100 parts by weight of the rubber.

10 2. A rubber mixture as claimed in Claim 1, which additionally contains—per 100 parts by weight of rubber—from 0.5 to 10 parts by weight of at least one organosilane corresponding to the following formulae: 10



and/or



in which R and R¹, which may be the same or different, each represent an alkyl group containing from 1 to 4 carbon atoms, a cycloalkyl group containing from 5 to 8 carbon atoms or a phenyl radical, n is 0, 1 or 2, Alk represents a difunctional, straight-chain or branched hydrocarbon radical containing from 1 to 10 carbon atoms and x is a number of from 2.0 to 8.0 or a hydrolysate and/or a condensate thereof.

20 3. A rubber mixture as claimed in Claim 1 or 2, wherein it contains a master batch of at least one organosilane corresponding to formula I, and/or a hydrolysate and/or a condensate of the organosilane I and a silicate filler and/or carbon black. 20

4. A rubber mixture as claimed in Claim 3, wherein it contains a master batch of 3-chloropropyl triethoxy silane, and/or a hydrolysate and/or condensate thereof and a silica filler obtained by precipitation in aqueous medium with a specific surface (DIN 66 132) of from 100 to 250 m²/g. 25

5. A rubber mixture as claimed in Claim 4, wherein it contains a master batch of 3-chloropropyl triethoxy silane, and/or a hydrolysate and/or condensate thereof and carbon black.

6. A rubber mixture as claimed in any of Claims 2 to 5, wherein it contains a master batch of at least one organosilane of formula II and/or III, a hydrolysate and/or condensate of the organosilane of formula II and/or III and a silica filler obtained by precipitation in aqueous medium and/or carbon black. 30

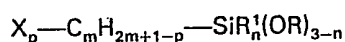
7. A rubber mixture as claimed in Claim 6, wherein it contains a master batch of at least one bis-(3-triethoxysilylpropyl)-oligosulphide containing from 2 to 8 sulphur atoms in the molecule, and/or a hydrolysate and/or condensate thereof, at least one silica filler obtained by precipitation in aqueous medium with a specific surface (as measured in accordance with DIN 66 132) of from 100 to 250 m²/g and/or at least one carbon black. 35

8. A rubber mixture as claimed in Claim 6 or 7, wherein the master batch of silane, its hydrolysate and/or condensate and silicate filler additionally contains from 0.2 to 10 parts by weight per 100 parts by weight of silica filler of at least one polyhydric alcohol.

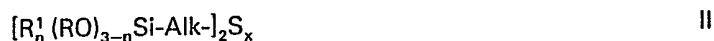
9. A rubber mixture as claimed in Claim 8, wherein the mixture contains as polyhydric alcohol ethylene glycol, propylene glycol, diethylene glycol, a polyethylene glycol, glycerol, hexane triol and/or glycidol. 40

10. A rubber mixture containing a silane of formula (I) as herein defined substantially as described with particular reference to any of the Examples.

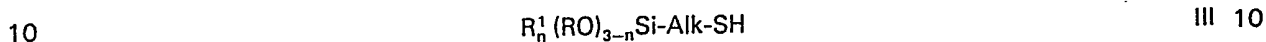
11. A process for vulcanising a rubber mixture by heating the mixture after forming to temperatures from 100 to 250°C for a period of time, dependant on the heating temperature, of from 1 to 200 minutes, the rubber mixture comprising at least one vulcanisable halogen-free rubber or of a mixture of one or more halogen-free rubbers with at most 80%, based on the total weight of the rubber, of at least one halogen-containing rubber, at least one silicate filler in quantities of from 1 to 250 parts by weight; at least one oxide of the metals zinc, magnesium and lead in quantities of from 0 to 15 parts by weight; at least one monobasic fatty acid containing from 12 to 24 carbon atoms in the alkyl chain, benzoic acid or salicylic acid in quantities of from 0 to 10 parts by weight; optionally sulphur and/or sulphur donors in quantities of from 0.1 to 15 parts by weight; at least one vulcanisation accelerator in quantities of from 0.1 to 10 parts by weight; at least one plasticiser in quantities of from 0 to 100 parts by weight; at least one stabiliser from the group comprising anti-agers, anti-fatigue agents, oxidation inhibitors, light stabilisers and anti-ozonants in respective quantities of from 0 to 10 parts by weight; carbon black in quantities of from 0 to 150 parts by weight; and having uniformly distributed therein from 0.1 to 20 parts by weight of at least one organosilane corresponding to the following general formula 55



- in which X represents chlorine or bromine, p is 1 or 2, m is 1 to 5, R¹ represents a C₁—C₅-alkyl group, a C₅—C₈-cycloalkyl group or a phenyl group, R represents a C₁—C₅-alkyl group, a C₅—C₈-cycloalkyl group, a methoxyethyl group, a phenyl group or a benzyl group and n is 0, 1 or 2, or a hydrolysate and/or a condensate thereof, all the quantities specified being based on 100 parts by weight of the rubber. 5
12. A process as claimed in Claim 11, wherein from 0.5 to 10 parts by weight—per 100 parts by weight of rubber—of at least one organosilane corresponding to the formulae



and/or



- in which R and R¹ which may be the same or different, each represent an alkyl group containing from 1 to 4 carbon atoms, a cycloalkyl group containing from 5 to 8 carbon atoms or a phenyl radical, n is 0, 1 or 2, Alk represents a difunctional, straight-chain or branched hydrocarbon radical containing from 1 to 10 carbon atoms and x is a number of from 2.0 to 8.0, or a hydrolysate and/or a condensate thereof, is additionally incorporated in the rubber mixture. 15

13. A process as claimed in Claims 11 or 12, wherein a master batch of at least one organosilane corresponding to formula I, and/or its hydrolysate and/or condensate and a silicate filler and/or a rubber-grade carbon black is worked into and uniformly distributed in the rubber mixture of parts thereof.

14. A process as claimed in Claim 12, wherein the master batch is a mixture of 3-chloropropyl triethoxy silane, and/or its hydrolysate and/or condensate and a silica filler obtained by precipitation in aqueous medium. 20

15. A process as claimed in any of Claims 11 to 14, wherein a master batch of at least one organosilane corresponding to formulae II and/or III, and/or a hydrolysate and/or a condensate of the organosilane II and/or III and a silica filler obtained by precipitation in aqueous medium and/or carbon black is incorporated in the rubber mixture. 25

16. A process as claimed in Claim 15, wherein a master batch of at least one bis-(3-triethoxysilylpropyl)oligosulphide containing from 2 to 6 sulphur atoms in the molecule, and/or a hydrolysate and/or condensate thereof, at least one silica filler obtained by precipitation in aqueous medium with a specific surface of from 100 to 250 m²/g and/or at least one rubber grade carbon black is incorporated in the rubber mixture. 30

17. A process for vulcanising a rubber mixture containing a silane of formula (I) as herein defined, substantially as described with particular reference to any of the Examples.

18. A rubber vulcanisate when produced by a process as claimed in any of claims 11 to 17.

19. A rubber vehicle tyre when produced using a vulcanisable rubber mixture as claimed in any of claims 1 to 10 or a vulcanisation process as claimed in any of claims 11 to 17. 35

20. A motor vehicle tyre having a tread produced using a vulcanisable rubber mixture as claimed in any of claims 1 to 10 or a vulcanisation process as claimed in any of claims 11 to 17.

21. An industrial rubber product or shoe sole when produced using a vulcanisable rubber mixture as claimed in any of claims 1 to 10 or a vulcanisation process as claimed in any of claims 11 to 17.