ORIGINAL

Title (EN) ARTICLE, IN PARTICULAR A PNEUMATIC TIRE, HAVING AN EXTERNAL RUBBER MIXTURE COMPRISING A LANTHANIDE SALT

Abstract: (EN)This invention relates to an article, in particular a pneumatic tire for a vehicle, comprising at least one external rubber mixture, in particular a tread, said external mixture comprising a rubber mixture consisting of at least one diene elastomer such as BR, SBR or NR, a reinforcing filler such as silica, a crosslinking system such as a vulcanization system, between 0.2 and 10 pce of an antioxidant, for example a substituted paraphenylenediamine, and between 0.2 and 10 pce of a lanthanide acetylacetonate such as a neodymium acetylacetonate. The latter makes it possible to advantageously reduce the consumption of antioxidant during the thermal oxidizing aging of the composition and hence of the external mixture.

Claims

1. Article comprising at least an external mixture made of rubber, the said external mixture comprising a rubber composition based on at least a diene elastomer, a reinforcing filler, a crosslinking system, between 0.2 and 10 phr of an antioxidant and between 0.2 and 10 phr of lanthanide acetylacetonate.

2. Article according to Claim 1, in which the diene elastomer is chosen from the group consisting of polybutadienes, natural rubber, synthetic polyisoprenes, butadiene copolymers, isoprene copolymers and the mixtures of these elastomers.

3. Article according to Claim 1 or 2, in which the reinforcing filler is chosen from the group consisting of carbon black, inorganic fillers and the mixtures of such fillers.

4. Article according to Claim 3, in which the reinforcing filler is silica, carbon black or a mixture of silica and carbon black.

5. Article according to any one of Claims 1 to 4, in which the level of reinforcing filler is between 30 and 150 phr.

6. Article according to any one of Claims 1 to 5, in which the crosslinking system is based on sulphur and on an accelerator.

7. Article according to any one of Claims 1 to 6, in which the level of lanthanide acetylacetonate is between 0.3 and 6 phr.

8. Article according to Claim 7, in which the level of lanthanide acetylacetonate is within a range from 0.5 to 4.0 phr.

9. Article according to any one of Claims 1 to 8, in which the lanthanide is chosen from the group consisting of lanthanum, cerium, praseodymium, neodymium, samarium, erbium and the mixtures of these rare earth metals.

10. Article according to Claim 9 , in which the lanthanide is neodymium.

11. Composition according to any one of Claims 1 to 10, in which the antioxidant is chosen from the group consisting of substituted p-phenylenediamines, substituted diphenylamines, substituted triphenylamines, quinoline derivatives and the mixtures of such compounds.

12. Article according to Claim 11, in which the antioxidant is chosen from the group consisting of substituted p-phenylenediamines and the mixtures of such diamines.

13. Article according to any one of Claims 1 to 12, in which the level of antioxidant is between 0.3 and 6 phr.

14. Article according to any one of Claims 1 to 13, characterized in that the said article is a tyre.

15. Tyre according to Claim 14, in which the external rubber mixture is composed of the tread of the said tyre.

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Sheet 1 of 1

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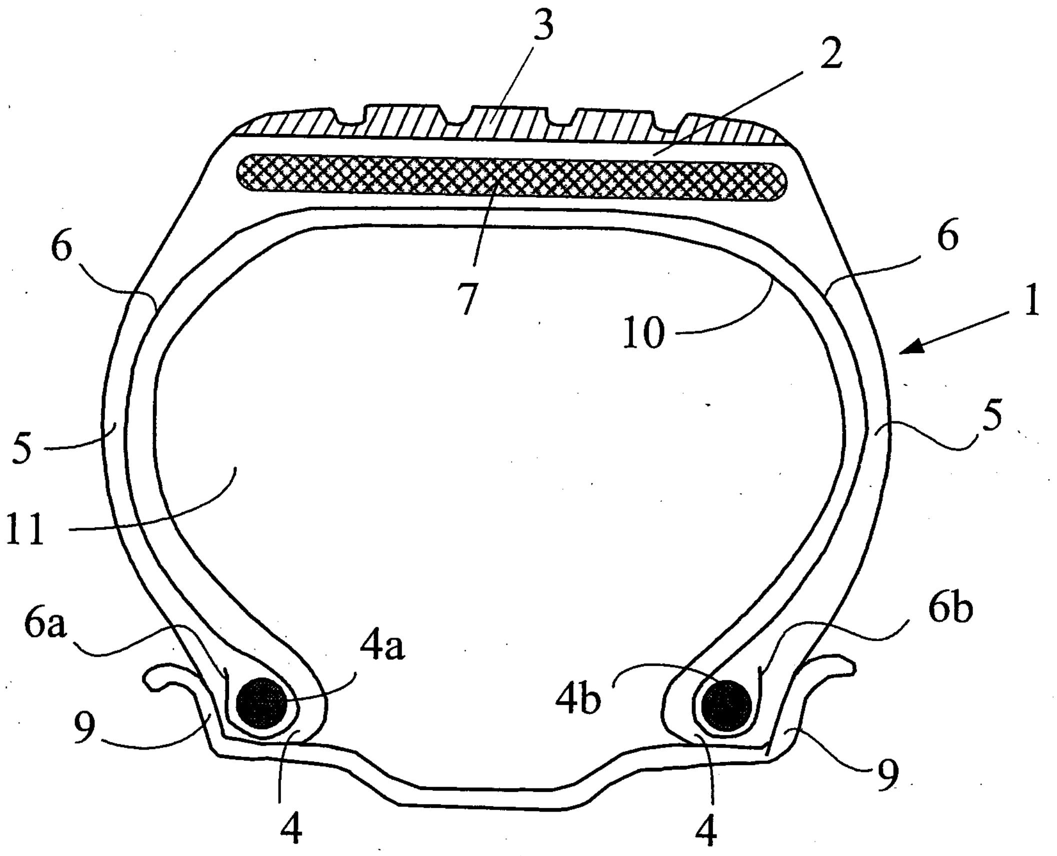
Figure



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P10-2384

ARTICLE, IN PARTICULAR A PNEUMATIC TYRE, HAVING AN EXTERNAL RUBBER MIXTURE COMPRISING A LANTHANIDE SALT

1. FIELD OF THE INVENTION

The field of the present invention is that of finished articles made of rubber, in particular vehicle tyres, and mixtures or profiled elements made of rubber used in the manufacture of such articles or tyres.

The present invention relates more particularly to antidegradant agents used to protect these rubber mixtures against the ageing due to oxidation when they are in contact with the air.

2. STATE OF THE ART

As is known, essentially unsaturated diene rubber vulcanisates, both natural and synthetic, due to the presence of double bonds on their molecular chains, are liable, if they are not protected, to deteriorate more or less rapidly after prolonged exposure to the atmosphere, due to known oxidation mechanisms. These complex mechanisms have been restated, for example, in the patent documents WO 99/02590 and WO 99/06480. They result, subsequent to cleavages of these double bonds and to the oxidation of the sulphur bridges, in a stiffening and a weakening of the vulcanisates, which damage is additionally accelerated under the joint action of heat, by “thermal-oxidation”, or also of that of light by “photo-oxidation”.

It has been possible to gradually inhibit these oxidation phenomena by virtue of the development and marketing of various antioxidants, including in particular p-phenylenediamine ("PPD" or "PPDA") derivatives, such as, for example, N-isopropyl-N'-phenyl-p-phenylenediamine ("I-PPD") or N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine ("6-PPD"), or quinoline derivatives ("TMQ"), simultaneously excellent antioxidants and antiozonants (see, for example, Patent Applications WO 2004/033548, WO 2005/063510 and WO 2005/133666). These antioxidants are today used systematically in diene rubber compositions, in particular in compositions for tyres, in order to combat ageing and premature wear of the latter.

The well-known disadvantage of these antioxidants is that their concentration in the rubber compositions naturally decreases over time due to their very chemical function and that they have, in addition, a strong natural propensity to migrate from the regions more concentrated in antioxidant towards the regions less concentrated in antioxidant, so much so that a person skilled in the art is led to use relatively large amounts of product, which is relatively expensive and furthermore harmful to the appearance of the finished products, due to a high staining power of a large number of antioxidants, in particular p-phenylenediamine derivatives.

In order to overcome the above disadvantages and thus to further improve the protection and the resistance to ageing of tyres, the proposal has in particular been made to incorporate, in these tyres, additional rubber layers having a high concentration of antioxidant, operating in a way as antioxidant reservoirs capable of delivering the antioxidant with the passage of time, by migration, as a function of the degree of depletion of the adjacent regions (see, for example, the patent documents WO 2009/029114, EP 1 319 527 or US 7 082 976).

The use of such antioxidant reservoirs, although effective, however exhibits the disadvantage of having to modify the internal structure of the tyres and consequently in particular of making it more complex and more expensive to manufacture them.

Consequently, the designers of diene rubber articles, in particular tyre manufacturers, are today looking for simple novel solutions which make it possible to overcome, at least in part, the abovementioned disadvantages.

3. BRIEF DESCRIPTION OF THE INVENTION

During their research studies, the Applicants have discovered a specific rubber formulation which, during the ageing thereof, has the distinguishing feature of consuming less antioxidant and which consequently makes it possible to meet the above objective.

Consequently, a first subject-matter of the invention is an article comprising at least an external mixture made of rubber, the said external mixture comprising a rubber composition based on at least a diene elastomer, a reinforcing filler, a crosslinking system, between 0.2 and 10 phr of an antioxidant and between 0.2 and 10 phr of lanthanide acetylacetonate.

By virtue of the presence of the above specific acetylacetonate, a significant reduction in the consumption of antioxidant has unexpectedly been observed in the rubber composition during the ageing of the latter.

The longevity of rubber vulcanisates can thus be improved, in particular that of tyres, which may be subjected, as is known, to particularly severe running conditions, in particular under a humid and corrosive atmosphere.

Application WO 2005/113666, filed by the Applicant Companies, had admittedly already described the specific use of lanthanide acetylacetonate in rubber compositions for tyres but in internal mixtures for the calendering of metal reinforcers (i.e., rubber plies reinforced with metal reinforcing elements) with the aim of improving the performance of adhesion of the metal to the rubber. However, the external mixtures for tyres to which we refer here, such as, for example, treads or sidewalls, are, in a known way, devoid of such metal reinforcers.

The present invention particularly relates to tyres intended to equip passenger motor vehicles, SUV (Sport Utility Vehicle) vehicles, two-wheel vehicles (in particular bicycles or motorcycles), aircraft, as well as industrial vehicles chosen from vans, heavy-duty vehicles – that is to say, underground, bus, heavy road transport vehicles (lorries, tractors, trailers) or off-road vehicles, such as agricultural vehicles or earth moving equipment – or other transportation or handling vehicles.

The invention and its advantages will be easily understood in the light of the description and implementational examples which follow and also of the single figure relating to these examples, which gives a diagrammatic representation, in radial cross section, of a tyre with a radial carcass reinforcement in accordance with the invention.

4. MEASUREMENTS AND TESTS USED

The rubber compositions are characterized, before and after curing, as indicated below.

4.1 - Mooney plasticity

Use is made of an oscillating consistometer as described in French Standard NF T 43-005 (1991). The Mooney plasticity measurement is carried out according to the following principle: the composition in the raw state (i.e., before curing) is moulded in a cylindrical chamber heated to 100°C. After preheating for one minute, the rotor rotates within the test specimen at 2 revolutions/minute and the working torque for maintaining this movement is measured after rotating for 4 minutes. The Mooney plasticity (ML 1+4) is expressed in "Mooney unit" (MU, with 1 MU = 0.83 N.m).

4.2 - Tensile tests

These tests make it possible to determine the elasticity stresses and the properties at break. Unless otherwise indicated, they are carried out in accordance with French Standard NF T 46-002 of September 1988. The modulus measurements were carried out under tension, unless expressly indicated otherwise, according to Standard ASTM D 412 of 1998 (test specimen "C"); the nominal secant moduli (or apparent stresses) are measured in second elongation (i.e., after a cycle of accommodation) at 10%, 100% and 300% elongation, respectively denoted MA10, MA100 and MA300 and expressed in MPa (standard conditions of temperature and hygrometry according to Standard ASTM D 1349 of 1999). The breaking stresses (in MPa) and the elongations at break (in %) are also measured. All these tensile measurements are carried out under standard conditions of temperature (23 ± 2°C) and hygrometry (50 ± 5% relative humidity), according to French Standard NF T 40-101 (December 1979).

5. DETAILED DESCRIPTION OF THE INVENTION

In the present description, unless expressly indicated otherwise, all the percentages (%) shown are % by weight. The abbreviation "phr" means parts by weight per hundred parts of elastomer or rubber (of the total of the elastomers, if several elastomers are present).

Moreover, any interval of values denoted by the expression "between a and b" represents the range of values greater than "a" and less than "b" (that is to say, limits a and b excluded), whereas any interval of values denoted by the expression "from a to b" means the range of values extending from "a" up to "b" (that is say, including the strict limits a and b).

The rubber article, in particular tyre, of the invention thus comprises at least an external rubber mixture comprising a rubber composition based (i.e., comprising the mixture or the reaction product) on at least a diene elastomer, a reinforcing filler, a crosslinking system and between 0.2 and 10 phr of an antioxidant; in addition, it has the novel and essential characteristic of comprising between 0.2 and 10 phr of a lanthanide acetylacetonate.

5.1 - Diene elastomer

The term "diene" (or indiscriminately rubber) elastomer is understood to mean, in a known way, an elastomer resulting at least in part (i.e., a homopolymer or a copolymer) from diene monomers (monomers bearing two carbon-carbon double bonds which may or may not be conjugated).

Diene elastomers can be classified in a known way into two categories: those said to be "essentially unsaturated" and those said to be "essentially saturated". Generally, the term "essentially unsaturated" diene elastomer is understood here to mean a diene elastomer resulting at least in part from conjugated diene monomers having a level of units of diene origin (conjugated dienes) which is greater than 15% (mol%). Thus it is, for example, that diene elastomers such as butyl rubbers or copolymers of dienes and of α-olefins of EPDM type do not come within the preceding definition and can in particular be described as "essentially saturated" diene elastomers (low or very low level of units of diene origin, always less than 15%). In the category of "essentially unsaturated" diene elastomers, the term "highly unsaturated" diene elastomer is understood to mean in particular a diene elastomer having a level of units of diene origin (conjugated dienes) which is greater than 50%.

Given these definitions, the term diene elastomer capable of being employed in the compositions in accordance with the invention is understood more particularly to mean:

(a) - any homopolymer obtained by polymerization of a conjugated diene monomer preferably having from 4 to 12 carbon atoms;

(b) - any copolymer obtained by copolymerization of one or more conjugated dienes with one another or with one or more vinylaromatic compounds preferably having from 8 to 20 carbon atoms;

(c) - a ternary copolymer obtained by copolymerization of ethylene and of an α-olefin preferably having from 3 to 6 carbon atoms with a non-conjugated diene monomer preferably having from 6 to 12 carbon atoms, such as, for example, the elastomers obtained from ethylene and propylene with a non-conjugated diene monomer of the abovementioned type, such as, in particular, 1,4-hexadiene, ethylidenenorbornene or dicyclopentadiene;

(d) - a copolymer of isobutene and of isoprene (butyl rubber) and also the halogenated versions, in particular chlorinated or brominated versions, of this type of copolymer.

Although it applies to any type of diene elastomer, a person skilled in the art of tyres will understand that the present invention is firstly employed with essentially unsaturated diene elastomers, in particular of the type (a) or (b) above.

More preferably, the diene elastomer is chosen from the group consisting of polybutadienes (BR), natural rubber (NR), synthetic polyisoprenes (IR), butadiene copolymers, isoprene copolymers and the mixtures of these elastomers. Such copolymers are more preferably chosen from the group consisting of butadiene/styrene copolymers (SBR), whether the latter are prepared by emulsion polymerization (ESBR) or in solution (SSBR), isoprene/butadiene copolymers (BIR), isoprene/styrene copolymers (SIR) and isoprene/butadiene/styrene copolymers (SBIR).

The elastomers can, for example, be block, random, sequential or microsequential elastomers and can be prepared in dispersion or in solution; they can be coupled and/or star-branched or also functionalized with a coupling and/or star-branching or functionalization agent. For coupling with carbon black, mention may be made, for example, of functional groups comprising a C-Sn bond or of aminated functional groups, such as benzophenone, for example; for coupling with a reinforcing inorganic filler, such as silica, mention may be made, for example, of silanol or polysiloxane functional groups having a silanol end (such as described, for example, in US 6 013 718), of alkoxysilane groups (such as described, for example, in US 5 977 238), of carboxyl groups (such as described, for example, in US 6 815 473 or US 2006/0089445) or of polyether groups (such as described, for example, in US 6 503 973). Mention may also be made, as other examples of such functionalized elastomers, of the elastomers (such as SBR, BR, NR or IR) of the epoxidized type.

The following are suitable: polybutadienes, in particular those having a content (molar %) of 1,2-units of between 4% and 80% or those having a content (molar %) of cis-1,4-units of greater than 80%, polyisoprenes, butadiene/styrene copolymers and in particular those having a Tg (glass transition temperature, measured according to Standard ASTM D3418) of between 0°C and -70°C and more particularly between -10°C and -60°C, and/or a styrene content of between 5% and 60% by weight and more particularly between 20% and 50%, a content (molar %) of 1,2-bonds of the butadiene part of between 4% and 75% and a content (molar %) of trans-1,4-bonds of between 10% and 80%, butadiene/isoprene copolymers, in particular those having an isoprene content of between 5% and 90% by weight and a Tg of -40°C to -80°C, or isoprene/styrene copolymers, in particular those having a styrene content of between 5% and 50% by weight and a Tg of between -25°C and -50°C. In the case of butadiene/styrene/isoprene copolymers, those having a styrene content of between 5% and 50% by weight and more particularly of between 10% and 40%, an isoprene content of between 15% and 60% by weight and more particularly between 20% and 50%, a butadiene content of between 5% and 50% by weight and more particularly of between 20% and 40%, a content (molar %) of 1,2-units of the butadiene part of between 4% and 85%, a content (molar %) of trans-1,4-units of the butadiene part of between 6% and 80%, a content (molar %) of 1,2- plus 3,4-units of the isoprene part of between 5% and 70% and a content (molar %) of trans-1,4-units of the isoprene part of between 10% and 50%, and more generally any butadiene/styrene/isoprene copolymer having a Tg of between -20°C and -70°C, are suitable in particular.

According to a specific embodiment, the predominant diene elastomer by weight (in particular for more than 50 phr) is an SBR, whether an SBR prepared in emulsion ("ESBR") or an SBR prepared in solution ("SSBR"), or an SBR/BR, SBR/NR (or SBR/IR), BR/NR (or BR/IR) or also SBR/BR/NR (or SBR/BR/IR) blend (mixture). This is the case in particular when the compositions of the invention are intended to constitute, in the tyres, rubber matrices of certain treads (for example for passenger vehicles). In the case of an SBR (ESBR or SSBR) elastomer, use is made in particular of an SBR having a moderate styrene content, for example of between 20% and 35% by weight, or a high styrene content, for example from 35 to 45%, a content of vinyl bonds of the butadiene part of between 15% and 70%, a content (molar %) of trans-1,4-bonds of between 15% and 75% and a Tg of between -10°C and

-55°C; such an SBR can advantageously be used as a mixture with a BR preferably having more than 90% (molar %) of cis-1,4-bonds.

According to another specific embodiment, the predominant diene elastomer by weight (in particular for more than 50 phr) is an isoprene elastomer. This is the case in particular when the rubber compositions described are intended to constitute, in the tyres, treads (in particular for industrial vehicles) or sidewalls.

The term "isoprene elastomer" is understood to mean, in a known way, an isoprene homopolymer or copolymer, in other words a diene elastomer chosen from the group consisting of natural rubber (NR), synthetic polyisoprenes (IR), the various copolymers of isoprene and the mixtures of these elastomers. Mention will in particular be made, among isoprene copolymers, of isobutene/isoprene copolymers (butyl rubber - IIR), isoprene/styrene copolymers (SIR), isoprene/butadiene copolymers (BIR) or isoprene/butadiene/styrene copolymers (SBIR). This isoprene elastomer is preferably natural rubber or a synthetic cis-1,4-polyisoprene; use is preferably made, among these synthetic polyisoprenes, of the polyisoprenes having a level (molar %) of cis-1,4-bonds of greater than 90%, more preferably still of greater than 98%.

According to another specific embodiment, in particular when it is intended for a tyre sidewall or for an airtight layer of a tubeless tyre (or other air-impermeable component), the rubber composition can comprise at least one essentially saturated diene elastomer, in particular at least one EPDM copolymer or one butyl rubber (optionally chlorinated or brominated), whether these copolymers are used alone or as a mixture with highly unsaturated diene elastomers as mentioned above, in particular NR or IR, BR or SBR.

According to another specific embodiment of the invention, the rubber composition comprises a blend of a (one or more) "high Tg" diene elastomer exhibiting a Tg of between -70°C and 0°C and of a (one or more) "low Tg" diene elastomer of between -110°C and -80°C, more preferably between -105°C and -90°C. The high Tg elastomer is preferably chosen from the group consisting of S-SBRs, E-SBRs, natural rubber, synthetic polyisoprenes (exhibiting a level (molar %) of cis-1,4-structures preferably of greater than 95%), BIRs, SIRs, SBIRs and the mixtures of these elastomers. The low Tg elastomer preferably comprises butadiene units according to a level (molar %) at least equal to 70%; it preferably consists of a polybutadiene (BR) exhibiting a level (molar %) of cis-1,4-structures of greater than 90%.

In conclusion, the rubber composition of the invention can comprise just one or several diene elastomers, it being possible for this diene elastomer or these diene elastomers in addition to be used in combination with any type of synthetic elastomer other than a diene elastomer, indeed even with polymers other than elastomers, for example thermoplastic polymers.

5.2 - Reinforcing filler

The composition of the invention comprises any type of "reinforcing" filler known for its capabilities of reinforcing a rubber composition which can be used for the manufacture of tyres, for example an organic filler, such as carbon black, a reinforcing inorganic filler, such as silica, with which a coupling agent is combined in a known way, or a mixture of these two types of filler.

Such a reinforcing filler typically consists of nanoparticles, the mean size (by weight) of which is less than a micrometer, generally less than 500 nm, most often between 20 and 200 nm, in particular and more preferably between 20 and 150 nm.

Preferably, the level of total reinforcing filler (in particular of silica or of carbon black or a mixture of silica and carbon black) is between 30 and 150 phr. Above 150 phr, there exists a risk of increase in the hysteresis and thus in the rolling resistance of the tyres. For this reason, the level of total reinforcing filler is more preferably comprised within a range from 40 to 120 phr.

As particularly preferred example, in particular for use in a tyre tread, use is made of 40 to 150 phr, in particular of 50 to 120 phr, of carbon black, of silica, or of a mixture of silica and carbon black.

All carbon blacks, in particular blacks conventionally used in tyres or their treads ("tyre-grade" blacks), are suitable as carbon blacks. Mention will more particularly be made, among the latter, of the reinforcing carbon blacks of the 100, 200 or 300 series, or the blacks of the 500, 600 or 700 series (ASTM grades), such as, for example, the N115, N134, N234, N326, N330, N339, N347, N375, N550, N683 or N772 blacks. The carbon blacks might, for example, be already incorporated in the diene, in particular isoprene, elastomer in the form of a masterbatch (see, for example, Applications WO 97/36724 or WO 99/16600).

Mention may be made, as examples of organic fillers other than carbon blacks, of the functionalized polyvinyl organic fillers as described in Applications WO-A- 2006/069792, WO-A- 2006/069793, WO-A-2008/003434 and WO-A-2008/003435.

The term "reinforcing inorganic filler" should be understood here as meaning any inorganic or mineral filler, whatever its colour and its origin (natural or synthetic), also known as "white filler", "clear filler" or even "non-black filler" in contrast to carbon black, capable of reinforcing by itself, without means other than an intermediate coupling agent, a rubber composition intended for the manufacture of tyres, in other words capable of replacing, in its reinforcing role, a conventional tyre-grade carbon black; such a filler is generally characterized, in a known way, by the presence of hydroxyl (-OH) groups at its surface.

Mineral fillers of the siliceous type, preferably silica (SiO_2), are suitable in particular as reinforcing inorganic fillers. The silica used can be any reinforcing silica known to a person skilled in the art, in particular any precipitated or pyrogenic silica exhibiting a BET surface and a CTAB specific surface both of less than 450 m^2/g, preferably from 30 to 400 m^2/g, in particular between 60 and 300 m^2/g. Mention will be made, as highly dispersible precipitated silicas ("HDS"), for example, of the "Ultrasil" 7000 and "Ultrasil" 7005 silicas from Degussa, the "Zeosil" 1165MP, 1135MP and 1115MP silicas from Rhodia, the "Hi-Sil" EZ150G silica from PPG or the "Zeopol" 8715, 8745 and 8755 silicas from Huber.

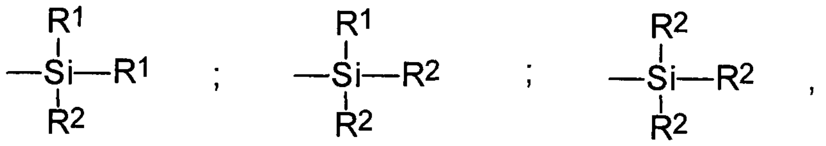
In order to couple the reinforcing inorganic filler to the diene elastomer, use is made, in a well-known way, of an at least bifunctional coupling agent (or bonding agent) intended to provide a satisfactory connection, of chemical and/or physical nature, between the inorganic filler (surface of its particles) and the diene elastomer. Use is made, in particular, of at least bifunctional organosilanes or polyorganosiloxanes.

Use is made in particular of silane polysulphides, referred to as "symmetrical" or "asymmetrical" depending on their specific structure, as described, for example, in Applications WO 03/002648 (or US 2005/016651) and WO 03/002649 (or US 2005/016650).

Silane polysulphides corresponding to the following general formula (I):

(I) $Z - A - S_x - A - Z$, in which:

- x is an integer from 2 to 8 (preferably from 2 to 5);
- the symbols A, which are identical or different, represent a divalent hydrocarbon radical (preferably a C_1-C_{18} alkylene group or a C_6-C_{12} arylene group, more particularly a C_1-C_{10}, in particular a C_1-C_4, alkylene, especially propylene);
- the symbols Z, which are identical or different, correspond to one of the three formulae below:



$$-\overset{R1}{\underset{R2}{Si}}-R1 \quad ; \quad -\overset{R1}{\underset{R2}{Si}}-R2 \quad ; \quad -\overset{R2}{\underset{R2}{Si}}-R2 \quad ,$$

in which:

- the R^1 radicals, which are unsubstituted or substituted and identical to or different from one another, represent a C_1-C_{18} alkyl, C_5-C_{18} cycloalkyl or C_6-C_{18} aryl group (preferably, C_1-C_6 alkyl, cyclohexyl or phenyl groups, in particular C_1-C_4 alkyl groups, more particularly methyl and/or ethyl),
- the R^2 radicals, which are unsubstituted or substituted and identical to or different from one another, represent a C_1-C_{18} alkoxyl or C_5-C_{18} cycloalkoxyl group (preferably a group chosen from C_1-C_8 alkoxyls and C_5-C_8 cycloalkoxyls, more preferably still a group chosen from C_1-C_4 alkoxyls, in particular methoxyl and ethoxyl),

are suitable in particular, without the above definition being limiting.

In the case of a mixture of alkoxysilane polysulphides corresponding to the above formula (I), in particular normal commercially available mixtures, the mean value of the "x" symbols is a fractional number preferably of between 2 and 5, more preferably approximately 4. However, the invention can also advantageously be employed, for example, with alkoxysilane disulphides ($x = 2$).

Mention will more particularly be made, as examples of silane polysulphides, of bis((C_1-C_4)alkoxyl(C_1-C_4) alkylsilyl(C_1-C_4)alkyl) polysulphides (in particular disulphides, trisulphides or tetrasulphides), such as, for example, bis(3-trimethoxysilylpropyl) or bis(3-triethoxysilylpropyl) polysulphides. Use is in particular made, among these compounds, of bis(3-triethoxysilylpropyl) tetrasulphide, abbreviated to TESPT, of formula $[(C_2H_5O)_3Si(CH_2)_3S_2]_2$, or bis(triethoxysilylpropyl) disulphide, abbreviated to TESPD, of formula $[(C_2H_5O)_3Si(CH_2)_3S]_2$. Mention will also be made, as preferred examples, of bis(mono(C_1-C_4)alkoxyldi(C_1-C_4)alkylsilylpropyl) polysulphides (in particular disulphides, trisulphides or tetrasulphides), more particularly bis(monoethoxydimethylsilylpropyl) tetrasulphide, such as described in the abovementioned Patent Application WO 02/083782 (or US 7 217 751).

Mention will in particular be made, as example of coupling agents other than an alkoxysilane polysulphide, of bifunctional POSs (polyorganosiloxanes) or of hydroxysilane polysulphides ($R^2 = OH$ in the above formula I), such as described, for example, in Patent Applications WO 02/30939 (or US 6 774 255), WO 02/31041 (or US 2004/051210) and WO 2007/061550, or of silanes or POSs carrying azodicarbonyl functional groups, such as described, for example, in Patent Applications WO 2006/125532, WO 2006/125533 and WO 2006/125534.

Mention will be made, as examples of other silane sulphides, for example, of the silanes carrying at least one thiol (-SH) functional group ("mercaptosilanes") and/or at least one masked thiol functional group, such as described, for example, in Patents or Patent Applications US 6 849 754, WO 99/09036, WO 2006/023815 and WO 2007/098080.

Of course, use might also be made of mixtures of the coupling agents described above, as described in particular in the abovementioned Application WO 2006/125534.

In the rubber compositions of the invention, when they are reinforced by an inorganic filler, such as silica, the content of coupling agent is preferably between 2 and 15 phr, more preferably between 3 and 12 phr.

A person skilled in the art will understand that a reinforcing filler of another nature, in particular organic nature, such as carbon black, might be used as filler equivalent to the reinforcing inorganic filler described in the present section, provided that this reinforcing filler is covered with an inorganic layer, such as silica, or else comprises, at its surface, functional sites, in particular hydroxyls, requiring the use of a coupling agent in order to form the connection between the filler and the elastomer. By way of example, mention may be made, for example, of carbon blacks for tyres, such as described, for example, in the patent documents WO 96/37547 and WO 99/28380.

According to another particularly preferred embodiment, use is made, as predominant filler, of a reinforcing inorganic filler, in particular silica, at a level within a range from 70 to 120 phr, to which reinforcing inorganic filler can advantageously be added carbon black at a minor level at most equal to 15 phr, in particular within a range from 1 to 10 phr.

5.3 - Crosslinking system

The crosslinking system is preferably a vulcanisation system, that is to say a system based on sulphur (or on a sulphur-donating agent) and on a primary vulcanisation accelerator. Various known vulcanisation activators or secondary accelerators, such as zinc oxide, stearic acid or equivalent compounds, or guanidine derivatives (in particular diphenylguanidine), incorporated during the first non-productive phase and/or during the productive phase, as described subsequently, are additional to this base vulcanisation system.

The sulphur is used at a preferable level of between 0.5 and 12 phr, in particular between 1 and 10 phr. The primary vulcanisation accelerator is used at a preferable level of between 0.5 and 10 phr, more preferably of between 0.5 and 5.0 phr.

Use may be made, as (primary or secondary) accelerator, of any compound capable of acting as accelerator for the vulcanisation of diene elastomers in the presence of sulphur, in particular accelerators of the type of the thiazoles and their derivatives, or accelerators of the types of zinc dithiocarbamates or thiurams. These accelerators are, for example, chosen from the group consisting of 2-mercaptobenzothiazyl disulphide (abbreviated to "MBTS"), tetrabenzylthiuram disulphide ("TBZTD"), N-cyclohexyl-2-benzothiazolesulphenamide ("CBS"), N,N-dicyclohexyl-2-benzothiazolesulphenamide ("DCBS"), N-(tert-butyl)-2-benzothiazolesulphenamide ("TBBS"), N-(tert-butyl)-2-benzothiazolesulphenimide ("TBSI"), zinc dibenzyldithiocarbamate ("ZBEC") and the mixtures of these compounds.

5.4 - Antioxidant

The composition of the invention has the characteristic of comprising between 0.2 and 10 phr of an antioxidant, preferably between 0.3 and 6 phr and more preferably within a range from 0.5 to 4 phr of such an antioxidant.

The antioxidant used in the composition of the invention is any antioxidant known to be effective in preventing ageing of rubber vulcanisates attributable to the action of the oxygen.

Mention may in particular be made of derivatives of para-phenylenediamine (abbreviated to "PPD" or "PPDA"), also called, in a known way, substituted para-phenylenediamines, such as, for example, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (better known under the abbreviated term "6-PPD"), N-isopropyl-N'-phenyl-p-phenylenediamine (abbreviated to "I-PPD"), phenyl-cyclohexyl-p-phenylenediamine, N,N'-di(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-diaryl-p-phenylenediamine ("DTPD"), diaryl-p-phenylenediamine ("DAPD"), 2,4,6-tris[N-(1,4-dimethylpentyl)-p-phenylenediamino]-1,3,5-triazine, and the mixtures of such diamines.

Mention may also be made of derivatives of quinoline ("TMQ"), such as, for example, 1,2-dihydro-2,2,4-trimethylquinoline and 6-ethoxy-1,2-dihydro-2,2,4- trimethylquinoline.

Mention may also be made of substituted diphenylamines or triphenylamines, such as described, for example, in Applications WO 2007/121936 and WO 2008/055683, in particular 4,4'-bis(isopropylamino)triphenylamine, 4,4'-bis(1,3-dimethylbutylamino)triphenylamine or 4,4'-bis(1,4-dimethylpentylamino)triphenylamine.

Mention may also be made of dialkyl thiodipropionates or also of phenolic antioxidants, in particular of the family of the 2,2'-methylenebis[4-(C_1-C_{10})alkyl-6-(C_1-C_{12})alkyl-phenols], such as described in particular in the abovementioned Application WO 99/02590.

Of course, in the present description, the term "antioxidant" can denote both a single antioxidant compound or a mixture of several antioxidant compounds.

Preferably, the antioxidant is chosen from the group consisting of substituted p-phenylenediamines, substituted diphenylamines, substituted triphenylamines, quinoline derivatives and the mixtures of such compounds; more preferably still, the antioxidant is chosen from the group consisting of substituted p-phenylenediamines and the mixtures of such diamines.

5.5 - Acetylacetonate

An essential characteristic of the composition of the external mixture is that it comprises between 0.2 and 10 phr of lanthanide acetylacetonate.

Below 0.2 phr, there is a risk of the targeted technical effect being inadequate, whereas, above 10 phr, the costs increase and the risk exists of a deterioration in certain mechanical properties of the compositions, in the initial state and after ageing. For these various reasons, the said level of lanthanide acetylacetonate is preferably between 0.3 and 6 phr, more preferably still within a range from 0.5 to 4.0 phr.

It should be remembered that the term of "lanthanide" is reserved for the metals, referred to as "rare earth metals", the atomic number of which varies from 57 (lanthanum) to 71 (lutetium).

Preferably, the lanthanide is chosen from the group consisting of lanthanum, cerium, praseodymium, neodymium, samarium, erbium and the mixtures of these rare earth metals. Use is more preferably made of cerium, samarium or neodymium, in particular neodymium.

It should be remembered here that lanthanide salts have been used essentially to date as catalysts for the polymerization of polymers or elastomers, such as dienes (see, by way of examples, US-A-3 803 053, US-A-5 484 897, US-A-5 858 903, US-A-5 914 377 or US-B-6 800 705). They have also been described as promoters of metal/rubber adhesion in internal mixtures for the calendering of metal reinforcers (see abovementioned Application WO 2005/113666).

5.6 - Other constituents

The rubber compositions can also comprise all or a portion of the additives generally used in rubber compositions intended to constitute external mixtures for finished articles made of rubber, such as tyres, such as, for example, plasticizing agents or extending oils, whether the latter are aromatic or nonaromatic in nature, in particular very slightly aromatic or nonaromatic oils (e.g., paraffinic oils, or naphthenic oils which are hydrogenated, MES oils or TDAE oils), vegetable oils, ether plasticizers, ester plasticizers (for example, glycerol trioleates), fillers other than those mentioned above, for example lamellar fillers, plasticizing hydrocarbon resins exhibiting a high Tg, preferably of greater than 30°C, such as described, for example, in Applications WO 2005/087859, WO 2006/061064 and WO 2007/017060, other antidegradant or antiageing agents, such as, for example, antiozonants, vulcanisation accelerators, activators or retarders, methylene acceptors and donors (for example, resorcinol, HMT or H3M) or other reinforcing resins. A person skilled in the art will know how to adjust the formulation of the compositions according to his specific requirements.

The abovementioned plasticizing hydrocarbon resins can be chosen in particular from the group consisting of cyclopentadiene homopolymer or copolymer resins, dicyclopentadiene homopolymer or copolymer resins, terpene homopolymer or copolymer resins, terpene-phenol homopolymer or copolymer resins, C_5 fraction homopolymer or copolymer resins, C_9 fraction homopolymer or copolymer resins, α-methylstyrene homopolymer or copolymer resins and the mixtures of these resins.

The rubber compositions can also comprise coupling activators, when a coupling agent is used, agents for covering the inorganic filler when an inorganic filler is used, or more generally processing aids capable, in a known way, by virtue of an improvement in the dispersion of the filler in the rubber matrix and of a lowering in the viscosity of the compositions, of improving their property of processing in the raw state. These covering agents are well known (see, for example, Patent Applications WO 2006/125533, WO 2007/017060 and WO 2007/003408); mention will be made, for example, of hydroxysilanes or hydrolysable silanes, such as hydroxysilanes or alkylalkoxysilanes, in particular alkyltriethoxysilanes, such as, for example, (1-octyl)triethoxysilane, polyols (for example, diols or triols), polyethers (for example, polyethylene glycols), primary, secondary or tertiary amines (for example trialkanolamines) or hydroxylated or hydrolysable polyorganosiloxanes (for example, α,ω-dihydroxypolyorganosilanes, in particular α,ω-dihydroxypolydimethylsiloxanes).

5.7 - Preparation of the rubber compositions

The compositions are manufactured in appropriate mixers using two successive preparation phases well known to a person skilled in the art: a first phase of thermomechanical working or kneading ("non-productive" phase) at high temperature, up to a maximum temperature of between 110°C and 190°C, preferably between 130°C and 180°C, followed by a second phase of mechanical working ("productive" phase) up to a lower temperature, typically of less than 110°C, finishing phase during which the crosslinking system is incorporated.

By way of example, the non-productive phase is carried out in a single thermomechanical stage of a few minutes (for example, between 2 and 10 min) during which all the base constituents necessary and other additives, with the exception of the crosslinking or vulcanisation system, are introduced into an appropriate mixer, such as a normal internal mixer. After cooling the mixture thus obtained, the vulcanisation system is then incorporated in an external mixer, such as an open mill, maintained at low temperature (for example, between 30°C and 100°C). The combined mixture is then mixed (productive phase) for a few minutes (for example, between 5 and 15 min).

Preferably, lanthanide acetylacetonate is introduced during the non-productive phase, at the same time as the antioxidant. However, the invention also applies to the case where all or only a fraction of this acetylacetonate is introduced during the productive phase.

The final composition thus obtained can subsequently be calendered, for example in the form of a sheet, or else extruded, for example to form an external rubber profiled element for a tyre, such as, for example, a tread.

The vulcanisation (or curing) can subsequently be carried out in a known way at a temperature generally of between 130°C and 200°C, preferably under pressure, for a sufficient time which can vary, for example, between 5 and 90 min, depending in particular on the curing temperature, the vulcanisation system adopted and the vulcanisation kinetics of the composition under consideration.

The invention relates to the rubber articles, in particular the tyres, both in the "raw" state (i.e., before curing) and in the "cured" or vulcanised state (i.e., after vulcanisation).

6. EXAMPLES OF THE IMPLEMENTATION OF THE INVENTION

6.1 - Use of the rubber composition in a tyre

The rubber composition described above can preferably be used for the manufacture of any external mixture intended for a tyre for a motor vehicle.

"External" or "exterior" mixture is understood here to mean any part made of rubber of the tyre (more generally of a rubber article) which opens onto the outside of the said tyre, in other words which is in contact with the air or with an inflation gas; mention may be made, as examples, of the tread, sidewalls or airtight layer of the tyre.

"Internal" or "interior" mixture is understood to mean, in contrast, any part made of rubber of the tyre (more generally of a rubber article) which does not open onto the outside of the tyre, which is not in contact with the air or an inflation gas, in other words which is thus situated in the actual inside of the internal structure of the tyre; mention may be made, as examples, of the mixtures for the calendering of metal reinforcers present in the carcass reinforcement or the crown reinforcement of the tyre.

By way of example, the single appended figure represents, highly diagrammatically, a radial cross section of a tyre with radial carcass reinforcement in accordance with the invention, for example intended for a heavy duty vehicle or for a passenger vehicle in this general representation.

In this figure, the tyre (1) represented diagrammatically comprises a crown region (2) comprising a tread (3) (for simplification, comprising a very simple tread pattern) intended to come into contact with the road and two nonextendable beads (4) in which a carcass reinforcement (6) is anchored. The crown (2), joined to the said beads (4) via two sidewalls (5), is, in a way known per se, reinforced by a crown reinforcement or "belt" (7) at least partially made of metal and radially external with respect to the carcass reinforcement (6) passing through this crown region (2), this belt (7) being, for example, composed of at least two superimposed crossed plies reinforced by metal cords.

The carcass reinforcement (6) is anchored here in each bead (4) by winding around two bead threads (4a, 4b), the turn-up (6a, 6b) of this reinforcement (6) being, for example, positioned toward the outside of the tyre (1), which is here represented fitted to its wheel rim (9). The carcass reinforcement (6) is composed of at least one ply reinforced by textile or metal radial cords, that is to say that these cords are positioned virtually parallel to one another and extend from one bead to the other, so as to form an angle of between 80° and 90° with the median circumferential plane (plane perpendicular to the axis of rotation of the tyre which is situated at mid distance from the two beads 4 and passes through the middle of the crown reinforcement (7). Of course, this tyre (1) additionally comprises, in a known way, an airtight layer (10), which defines the radially internal face of the tyre and which is intended to protect the carcass ply from the diffusion of air or another inflation gas originating from the space (11) interior to the tyre casing.

The tyre in accordance with the invention has the essential characteristic of comprising, in its structure, at least an external mixture according to the invention, constituting, for example, all or part of the tread (3), or of the sidewalls (5), or of the airtight layer (10).

6.2 - Ageing tests

For the requirements of this test, four rubber compositions (denoted hereinafter C-1 to C-4) were prepared, the formulation of which is given in Table 1, the levels of the various products being expressed in phr (part by weight per hundred parts of total elastomer, in this instance composed either of 100 phr of SBR, or of 75 phr of SBR and 25 phr of BR).

The control compositions (C-1 and C-3) essentially comprise, in a known way, in addition to the elastomer and the reinforcing filler (silica and carbon black), a silane coupling agent, a plasticizing system composed of an oil and of a thermoplastic hydrocarbon resin, an antioxidant, zinc oxide, stearic acid, guanidine derivative, sulphur and sulphenamide accelerator. These compositions are, for example, intended to constitute the tread of a tyre for a passenger vehicle.

The compositions according to the invention (respectively C-2 and C-4) differ from the two previous compositions (respectively C-1 and C-3) only in the additional presence alone of 2.0 phr of lanthanide acetylacetonate compound (neodymium).

These compositions were manufactured in the following way: the reinforcing filler (silica and carbon black), the diene elastomer (SBR or SBR/BR blend), an antioxidant, the various other plasticizers, if appropriate, the acetylacetonate, and also the various other ingredients, with the exception of the vulcanisation system, were successively introduced into an internal mixer, the initial vessel temperature of which was approximately 60°C; the mixer was thus approximately 70% filled (% by volume). Thermomechanical working (non-productive phase) was then carried out in a stage of approximately 2 to 4 min, until a maximum "dropping" temperature of 165°C was achieved. The mixture thus obtained was recovered and cooled and then sulphur and an accelerator of sulphenamide type were incorporated on an external mixer (homofinisher) at 30°C, the combined mixture being mixed (productive phase) for several minutes.

The compositions thus obtained are subsequently either calendered in the form of sheets (thickness of 2 to 3 mm) for the measurement of their physical or mechanical properties, on the one hand, and for carrying out the ageing tests, on the other hand.

The mechanical properties of these compositions have been listed in the appended Table 2. Before curing, it should first of all be noted that the two compositions in accordance with the invention have an advantageously reduced Mooney viscosity, an indicator of an improved processability. After curing (15 min at 160°C), the four compositions have equivalent properties, apart from an elongation at break which is advantageously greater in the presence of the acetylacetonate (compositions C-2 and C-4 in accordance with the invention).

After curing the compositions, the rubber blocks are placed in an oven at a temperature of 55°C, under a relative humidity of 95%, for one to several weeks, in order to compare the kinetics of reduction in the level of antioxidant of the compositions during this accelerated ageing. The level of antioxidant was measured by a known HPLC (high performance liquid chromatography) technique, on the one hand in the initial state, on non-aged test specimens, that is to say directly on exiting from the curing, and, on the other hand, after ageing for one to six weeks.

The results obtained are given in the appended Table 3. The level of antioxidant in the compositions is expressed in relative units, the base 100 being selected for each control composition in the initial state (i.e., after exiting from the curing).

On reading this Table 3, it is first of all found that, unexpectedly, the presence of lanthanide acetylacetonate already makes it possible, immediately after curing (initial state), to substantially (approximately 9%) reduce the loss of antioxidant present in the composition.

In addition, after accelerated thermal ageing, it is noted that, whatever the duration of the ageing, the presence of the acetylacetonate makes it possible to reduce, in a noteworthy fashion, the consumption of antioxidant over time, in comparison with the control composition.

This reduction in consumption of antioxidant confers, on the compositions of the invention, an improved protection against thermo-oxidative ageing, as is attested by the additional results in Table 4, in which a change in the elongation at break, in other words the ability of the material to withstand a tensile strain, as a function of the ageing (55°C under relative humidity of 95%), has been reported.

The elongation at break properties are expressed in relative units, the base 100 being selected for each control composition in the initial state (i.e., after exiting from the curing). On reading this Table 4, it is clearly found that the presence of the lanthanide acetylacetonate already makes it possible, immediately after curing (initial state), to substantially (approximately 14%) reduce the loss in elongation at break of the composition.

In addition, after accelerated thermal ageing, it is noted that, whatever the duration of the ageing, the presence of the acetylacetonate makes it possible to reduce, in a noteworthy fashion, the loss in elongation at break over time, in comparison with the control composition.

In conclusion, the above thermal ageing tests clearly demonstrate that the addition of the lanthanide acetylacetonate, therefore operating as an antidegradant agent, makes it possible to substantially reduce the consumption of antioxidant in the rubber compositions, thus affording the vulcanisates and thus also the rubber articles and tyres comprising them a potentially improved longevity due to better protection against the ageing due to oxidation.

Table 1

Formulation of the rubber compositions (in phr) :	C-1	C-2	C-3	C-4
Diene elastomer (1)	100	100	75	75
Diene elastomer (2)	-	-	25	25
Silica (3)	80	80	90	90
Silane coupling agent (4)	6.6	6.6	7.4	7.4
Carbon black (5)	4	4	4	4
Plasticizing oil (6)	20	20	10	10
Plasticizing resin (7)	20	20	20	20
Antioxidant (8)	2	2	2	2
Neodymium acetylacetonate (9)	-	2	-	2
Antiozone wax	1.5	1.5	1.5	1.5
Zinc oxide	2	2	2	2
Stearic acid	2	2	2	2
Diphenylguanidine (10)	1.5	1.5	1.5	1.5
Sulphur	1.2	1.2	1.2	1.2
Sulphenamide accelerator (11)	2	2	2	2

(1) SSBR with 25% of styrene, 59% of 1,2- polybutadiene units and 20% of trans-1,4-polybutadiene units (Tg = -24°C); level expressed as dry SBR (SBR extended with MES oil);

(2) BR (Nd) with 0.7% of 1,2-; 1.7% of trans -1,4-; 98% of cis-1,4- (Tg = -105°C);

(3) Silica "Zeosil 1165 MP" from Rhodia, in the form of microbeads (BET and CTAB: approximately 150-160 m^2/g);

(4) TESPT ("Si69" from Degussa);

(5) N234 (Degussa);

(6) MES oil ("Catenex SNR" from Shell);

(7) Polylimonene resin ("Dercolyte L120" from DRT);

(8) N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine ("Santoflex 6PPD" from Flexsys);

(9) $C_{15}H_{21}NdO_6.xH_2O$ (Sigma-Aldrich – Product No. 460427);

(10) Diphenylguanidine (Perkacit DPG from Flexsys);

(11) N-Cyclohexyl-2-benzothiazolesulphenamide ("Santocure CBS" from Flexsys).

Table 2

Composition No:	C-1	C-2	C-3	C-4
Properties before curing:				
Mooney (MU)	107	101	96	85
Properties after curing:				
MA10 (MPa)	6.8	6.5	5.9	5.2
MA 100 (MPa)	2.1	1.6	2.0	1.6
MA 300 (MPa)	2.2	1.7	2.1	1.7
Breaking stress (MPa)	21.8	20.4	18.1	18.1
Elongation at break (%)	560	640	500	570

Table 3

% by weight of antioxidant in the rubber composition (in relative units)	C-1	C-2	C-3	C-4
Initial state (after curing)	100	109	100	109
After ageing for 2 weeks	81	96	80	84
After ageing for 4 weeks	64	86	60	74
After ageing for 9 weeks	34	58	34	57

Table 4

Elongation at break (in relative units) :	C-1	C-2	C-3	C-4
Initial state (after curing)	100	114	100	114
After ageing for 2 weeks	93	106	94	103
After ageing for 4 weeks	87	101	85	97
After ageing for 9 weeks	82	86	83	86