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(71) Applicant(s)
Compagnie Generale Des Etablissements Michelin - Michelin and Cie

(72) Inventor(s)
Didier Vasseur

(74) Agent/Attorney
WATERMARK PATENT and TRADEMARK ATTORNEYS,Locked Bag 5,HAWTHORN VIC 3122

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(71) Déposant *(pour tous les Etats désignés sauf US)*: COMPAGNIE GENERALE DES ETABLISSEMENTS MICHELIN – MICHELIN & CIE [FR/FR]; 12, cours Sablon, F–63040 Clermont–Ferrand Cedex 09 (FR).

(72) Inventeur; et

(75) Inventeur/Déposant *(US seulement)*: VASSEUR, Didier [FR/FR]; Rue Claudius Labrosse, F–63100 Clermont–Ferrand (FR).

(74) Mandataire: HIEBEL, Robert; Michelin & Cie, Service SGD/LG/PI–LAD, F–63040 Clermont–Ferrand Cedex 09 (FR).

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(54) Title: COLOUR RUBBER COMPOSITION FOR TYRE

(54) Titre: COMPOSITION DE CAOUTCHOUC DE PNEUMATIQUE COULEUR

(57) Abstract

The invention concerns a white, light–coloured or colour tyre rubber composition devoid of carbon black, comprising at least a diene elastomer, a reinforcing white or coloured filler, an anti–photooxidation protective system, characterised in that said protective system is based at least on: (A) a 2,2'–methylene–bis–[4–alk yl(C_1–C_{10})–6–alkyl(C_1–C_{12})phenol]; (B) a dialkylthiodipropionate whereof the alkyl radicals, identical or different are (C_1–C_{30}), preferably (C_8–C_{20}), radicals; (C) a 2–(2–hydroxyphenyl)benzotriazole; (D) a "HALS" amine derived from 2,2,6,6–tetramethylpiperidine.

(57) Abrégé

Composition de caoutchouc de pneumatique blanche, claire ou colorée et dépourvue de noir de carbone, comportant au moins un élastomère diénique, une charge renforçante blanche ou colorée, un système de protection anti–photo–oxydant, caractérisée en ce que ledit système de protection est à base d'au moins: (A) un 2,2'–méthylène–bis–[4–alkyle(C_1 à C_{10})–6–alkyle(C_1 à C_{12})phénol]; (B) un dialkylthiodipropionate dont les radicaux alkyles, identiques ou différents, sont des radicaux en C_1 à C_{30}, de préférence en C_8 à C_{20}; (C) un 2–(2–hydroxyphényl)benzotriazole; (D) une amine "HALS" dérivée de la 2,2,6,6–tétraméthylpipéridine.

A RUBBER COMPOSITION FOR A COLOURED TYRE

The present invention relates to rubber compositions for tyres, and also to the antidegradants intended to protect these compositions against photo-oxidising atmospheric ageing due to the combined action of oxygen and light.

It relates more particularly to the anti-photo-oxidising protection of white, clear or coloured diene rubber compositions, devoid of carbon black and reinforced by at least one white or coloured filler, in particular silica, such compositions being sulphur-vulcanisable and forming part of coloured tyres.

As is known, vulcanised rubber compositions of essentially unsaturated diene rubbers, both natural and synthetic, owing to the presence of double bonds on their molecular chains, are likely to deteriorate more or less rapidly after prolonged exposure to the atmosphere, if they are not protected, owing to known oxidation mechanisms. These complex mechanisms have been described, for example, in the following documents: ref. [1]: *"Antidegradants for tire applications"* in *"Tire compounding"*, Education Symposium No. 37 (ACS), Cleveland, Communication I, October 1995; ref. [2]: *"Non-blooming high performance antidegradants"*, Kautschuk Gummi Kunststoffe, Year 47, No. 4, 1994, 248-255; ref. [3]: *"Antioxidants"* in Encycl. Polym. Sci. and Eng., 2nd Edition, Vol. 2, 73-91. Following breaking of these double bonds and the oxidation of the sulphur bridges, they bring about stiffening and embrittlement of the vulcanised rubber compositions, which degradation is furthermore accelerated under the combined action of heat by "thermo-oxidation", or alternatively that of light by

"photo-oxidation" (see e.g. ref. [4]: *"Photooxydation and stabilization of polymers"*, Trends in Polym. Sci., Vol. 4, No. 3, 1996, 92-98; ref. [5]: *"Degradation mechanisms of rubbers"*, Int. Polym. Science and Technol., Vol. 22, No. 12, 1995, 47-57).

It has been possible gradually to inhibit these oxidation phenomena owing to the development and sale of various antioxidants, the most effective of which are, in known manner, derivatives of quinoline ("TMQ"), or derivatives of p-phenylenediamine ("PPD" or "PPDA") which are even more active than the former, such as, for example, N-1,3-dimethylbutyl-N'-phenyl-p-phenylene-diamine (6-PPD). These TMQ and PPD-type antidegradants, sometimes even associated with each other, are nowadays very widespread and used virtually systematically (see e.g. refs. [1] to [3] above) in conventional tyre rubber compositions, filled at least in part with carbon black which imparts thereto their characteristic black colour.

Since savings in terms of fuel and the necessity of protecting the environment have become a priority, and in particular since the publication of European Patent Application EP-A-0 501 227, the interest in silica-reinforced compositions has been widely revived. This application describes a sulphur-vulcanisable rubber composition reinforced preferably majoritarily by a special precipitated silica which makes it possible to manufacture a tyre having a substantially improved rolling resistance, without adversely affecting the other properties, in particular those of adhesion, endurance and wear resistance.

Recently published European Patent Application EP-A-0 810 258 discloses a novel diene rubber composition reinforced by another special white filler, in this

case a specific alumina (Al_2O_3) of high dispersibility, which also makes it possible to obtain tyres or treads having such an excellent compromise of contradictory properties.

Thus, it is henceforth possible to conceive of coloured tyres being sold which, for aesthetic reasons, in particular in the field of passenger vehicles, meet a real expectation of the users, while being able to provide them with a substantial saving in terms of fuel.

It so happens that the antioxidants described previously, which have been developed and optimised after many years of research into conventional black rubber compositions, are not suitable for protecting tyre rubber compositions filled exclusively with white fillers, in particular silica or alumina, because the majority thereof, and in particular the TMQ or PPD derivatives referred to above, are not light-fast; under the action of UV radiation, they undergo an adverse colour change and stain the rubber compositions, which does not allow their use to be envisaged in white, clear or coloured compositions. Furthermore, the absence of carbon black, which hitherto acted as a very effective UV absorber in conventional compositions, results in aggravating all the degradation processes described previously, in particular those of photo-oxidation.

It was therefore necessary, in order to be able to develop coloured tyres, to develop new systems for protecting against photo-oxidising ageing, which have compromises in terms of novel properties, different from those used for black tyres, in particular particularly effective against UV, while being light-

fast and non-staining with respect to the compositions to be protected.

During its research, the Applicant has discovered an anti-photo-oxidising protection system which meets the above demands, this system being compatible firstly with sulphur vulcanisation and secondly with the harsh conditions of use of tyres (temperature, fatigue due to dynamic stresses).

Consequently, a first subject of the invention consists in a white, clear or coloured tyre rubber composition devoid of carbon black, including at least one diene elastomer, a white or coloured reinforcing filler, an anti-photo-oxidising protection system, this composition being characterised in that said protection system is based on at least:

(A) a 2,2'-methylene-bis-[4-(C_1 to C_{10})alkyl-6-(C_1 to C_{12})alkylphenol];
(B) a dialkyl thiodipropionate, the alkyl radicals of which, which may be identical or different, are C_1 to C_{30} radicals, preferably C_8 to C_{20} radicals;
(C) a 2-(2-hydroxyphenyl)benzotriazole;
(D) an "HALS" amine derived from 2,2,6,6-tetramethyl piperidine.

The subject of the invention is also coloured tyres or coloured rubber articles for such tyres, when they include a rubber composition according to the invention, such articles being in particular treads, underlayers intended, for example, to be placed beneath these treads, sidewalls, protectors, beads, and more generally any rubber layer or ply which may form part of a tyre.

"Coloured" tyres or rubber articles are understood in the present description to mean tyres or rubber articles, at least part of which is of a colour other than the conventional black, including white.

Furthermore, the subject of the invention is a process for protecting a white, clear or coloured tyre rubber composition devoid of carbon black against photo-oxidising ageing, this process being characterised in that an anti-photo-oxidising system such as described above is incorporated by mixing with said composition before the vulcanisation thereof.

Finally, the subject of the invention is the use of an anti-photo-oxidising system as defined above for protecting these white, clear or coloured tyre rubber compositions against photo-oxidation.

The invention and its advantages will be readily understood in the light of the following description and examples of embodiment.

I. MEASUREMENTS AND TESTS USED

The properties of the rubber compositions are evaluated as indicated hereafter. In the photo-oxidation, thermo-oxidation and colorimetry tests, the test samples used are non-standardised test samples consisting of strips of rubber of dimensions (L x l x e) of (110 x 15 x 2.5), in mm (millimetres).

I-1. Tensile tests

These tests make it possible to determine the elasticity stresses and the breaking properties; those carried out on the cured mixes are effected in

accordance with the standard AFNOR-NF-T46-002 of September 1988. The secant moduli (in MPa) are measured at 10% elongation (M10) and 100% elongation (M100). Unless indicated otherwise in the text, all these tensile measurements are effected under normal conditions of temperature and humidity in accordance with the standard AFNOR-NF-T40-101 of December 1979.

I-2. Shore A hardness tests

These measurements make it possible to assess the hardness of the compositions after curing, in accordance with standard ASTM D 2240-86.

I-3. Hysteresis losses

The hysteresis losses (HL) are measured by rebound at 60°C at the sixth impact, and expressed in % in accordance with the following equation:

$$HL(\%) = 100\ [(W_0-W_1)/W_0],$$

in which W_0 = energy supplied; W_1 = energy released.

I-4. Photo-oxidation tests

The compositions in the cured state are subjected to accelerated photo-ageing in the following manner: one face of the test pieces is exposed for 12 days beneath 4 high-pressure mercury vapour lamps (MAZDA MA400) at 60°C, in a SEPAP 12/24 (MPC) enclosure.

Then the evolution of the mechanical and colorimetric properties is measured. In particular, the tensile tests after accelerated photo-ageing are effected by extensometry of the test samples at stresses of low elongations (10% and 25%), in a first elongation, on an

Inströn 1122 machine, at a low traction speed (10 mm/min). The stresses measured are referenced F10 and F25.

I-5. Thermo-oxidation tests

These tests make it possible to evaluate the resistance to thermo-oxidation of the materials tested. For this, the parameters M10, M100 and HL are measured, after thermo-oxidising ageing of 30 days, at a constant temperature of 70°C, in an air-ventilated oven.

I-6. Colorimetric tests

The colorimetric values are determined by means of a Microflash 200 D DATA COLOR spectrocolorimeter in D65/10 configuration (daylight; angle of observation 10°). The colorimetric properties are measured in known manner, in accordance with the instruction manual for the colorimeter (May 1995), by analysing the reflectance spectrum of the test pieces.

These measurements are transferred to the "CIE LAB" system of the 3 three-dimensional colorimetric coordinates L*, a*, b*, in which system:

- the a* axis represents the green-red chromaticity coordinate, with a scale from -100 (green) to +100 (red);
- the b* axis represents the blue-yellow chromaticity coordinate, with a scale from -100 (blue) to +100 (yellow);
- the L* axis represents the luminosity coordinate, with a scale from 0 (black) to 100 (white);

- $\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ represents the overall average colorimetric deviation of each sample relative to a non-aged control; the higher ΔE is, the more of its initial colour the composition has lost.

II. CONDITIONS OF CARRYING OUT THE INVENTION

In addition to the usual additives and possibly one (or more) colouring agent(s), the compositions according to the invention include at least one diene elastomer, a white or coloured filler as a reinforcing filler, an anti-photo-oxidising protection system which is light-fast and non-staining with respect to the compositions protected, said system comprising at least, in combination, the compounds A, B, C and D set forth above.

II-1. Diene elastomer

"Diene" elastomer or rubber is understood to mean, in known manner, an elastomer resulting at least in part (i.e. a homopolymer or a copolymer) from diene monomers (monomers bearing two double carbon-carbon bonds, whether conjugated or not).

Generally, "essentially unsaturated" diene elastomer is understood here to mean a diene elastomer resulting at least in part from conjugated diene monomers, having a content of members or units of diene origin (conjugated dienes) which is greater than 15% (mole %).

Thus, for example, diene elastomers such as butyl rubbers or copolymers of dienes and of alpha-olefins of the EPDM type do not fall within the preceding definition, and may in particular be described as

"essentially saturated" diene elastomers (low or very low content of units of diene origin which is always less than 15%).

Within the category of "essentially unsaturated" diene elastomers, "strongly unsaturated" diene elastomer is understood to mean in particular a diene elastomer having a content of units of diene origin (conjugated dienes) which is greater than 50%.

As previously indicated, the present invention relates first and foremost to the anti-photo-oxidising protection of the tyre compositions based on essentially unsaturated diene elastomers. Of the latter, homopolymers obtained by polymerisation of a conjugated diene monomer having 4 to 12 carbon atoms, and also copolymers obtained by copolymerisation of one or more conjugated dienes with one another or with one or more vinyl aromatic compounds having 8 to 20 carbon atoms are preferably used.

Suitable conjugated dienes are, in particular, 1,3-butadiene, 2-methyl-1,3-butadiene, the 2,3-di(C_1 to C_5 alkyl)-1,3-butadienes such as, for instance, 2,3-dimethyl-1,3-butadiene, 2,3-diethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-isopropyl-1,3-butadiene, an aryl-1,3-butadiene, 1,3-pentadiene and 2,4-hexadiene.

Suitable vinyl aromatic compounds are, in particular, styrene, ortho-, meta- and para-methylstyrene, the commercial mixture "vinyl-toluene", para-tertio-butylstyrene, the methoxy-styrenes, the chloro-styrenes, vinyl mesitylene, divinyl benzene and vinyl naphthalene.

The copolymers may contain between 99% and 20% by weight of diene units and between 1% and 80% by weight of vinyl aromatic units. The elastomers may have any microstructure, which is a function of the polymerisation conditions used, in particular of the presence or absence of a modifying and/or randomising agent and the quantities of modifying and/or randomising agent used. The elastomers may for example be block, statistical, sequenced or microsequenced elastomers, and may be prepared in dispersion or in solution.

Preferred are polybutadienes, particularly those having a content of between 4% and 80% 1,2 units and those having a content of cis-1,4 bonds of more than 80%, polyisoprenes, butadiene-styrene copolymers, and in particular those having a styrene content of between 5% and 50% by weight and, more particularly, between 20% and 40% by weight, a content of 1,2 bonds of the butadiene part of between 4% and 65%, and a content of trans-1,4 bonds of between 20% and 80%, butadiene-isoprene copolymers and in particular those having an isoprene content of between 5% and 90% by weight and a glass transition temperature (Tg) of -40°C to -80°C, isoprene-styrene copolymers and 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, there are suitable in particular those having a styrene content of between 5% and 50% and, more particularly, 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 between 20% and 40%, a content of 1,2 units of the butadiene part of between 4% and 85%, a content of trans-1,4 units of the

butadiene part of between 6% and 80%, a content of 1,2 plus 3,4 units of the isoprene part of between 5% and 70%, and a content 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.

Of course, the elastomer may be coupled and/or starred or alternatively functionalised with a coupling and/or starring or functionalising agent. The elastomer may also be natural rubber or a blend based on natural rubber with any synthetic elastomer, in particular a diene elastomer.

Particularly preferably, the diene elastomer of the composition according to the invention is selected from the group of strongly unsaturated diene elastomers which consists of polybutadienes, polyisoprenes or natural rubber, butadiene-styrene copolymers, butadiene-isoprene copolymers, isoprene-styrene copolymers, butadiene-styrene-isoprene copolymers, or a mixture of two or more of these compounds.

When the composition according to the invention is in the form of a tread, the diene elastomer is preferably a butadiene-styrene copolymer prepared in solution having a styrene content of between 20% and 30% by weight, a content of vinyl bonds of the butadiene part of between 15% and 65%, a content of trans-1,4 bonds of between 15% and 75% and a Tg of between -20°C and -55°C, this butadiene-styrene copolymer possibly being used in a mixture with a polybutadiene having preferably more than 90% cis-1,4 bonds.

II-2. Reinforcing filler

All white fillers (also referred to as clear fillers) capable of reinforcing, alone or in a mixture with each other, to a greater or lesser extent according to the intended applications, a tyre rubber composition are suitable as reinforcing fillers, such as silica, alumina, clays, hydrates or oxides of aluminium and/or magnesium, bentonite, talc, chalk, kaoline or titanium oxide.

Preferably, the amount of reinforcing filler is within a range from 30 to 150 phr (parts by weight to one hundred parts of elastomer (or rubber)), more preferably 30 to 100 phr, the optimum differing according to the intended applications: the level of reinforcement expected for a bicycle tyre, for example, is of course far less than that required for a tyre suitable for travelling at a sustained high speed, for example a motorcycle tyre, a tyre for a passenger vehicle or for a utility vehicle such as a heavy truck vehicle.

Preferably, in particular when the composition of the invention relates to such a tyre capable of travelling at high speed, silica (SiO_2) or alumina (Al_2O_3), or even the two together, form(s) the majority, that is to say, more than 50% by weight, of the total reinforcing filler. More preferably still, silica and/or alumina form more than 80% by weight of this total reinforcing filler.

Silica and/or alumina may form the entire reinforcing filler; nevertheless, other white fillers, depending on the intended applications, may advantageously represent a greater or lesser fraction of the reinforcing filler.

Thus, it has been noted that another white filler associated, for example, with silica or alumina may have the effect of opacifying colours, in other words reducing the clear, that is to say, more or less translucent, nature of the compositions filled with silica or alumina. This other white filler is preferably selected from among chalk, talc or kaolin, more preferably kaolin; it is preferably used in an amount of 2.5 to 12.5%, more preferably 5 to 10% (% by weight relative to the weight of silica and/or alumina), depending on the intended applications; for an amount of less than 2.5%, the effect is generally scarcely visible, whereas for amounts greater than 12.5% the mechanical properties of the vulcanised rubber compositions may decrease.

It has also been noted that the result of using titanium oxide (TiO_2) is to impart a pastel tone to the colours selected, which is particularly aesthetic; the amount of titanium oxide preferably varies from 0.5 to 7%, more preferably from 1 to 3% (% by weight relative to the weight of silica and/or alumina), depending on the intended applications. For an amount less than 0.5%, the effect is generally scarcely visible, whereas for amounts greater than 7% there is the risk of blooming on the surface of the vulcanised rubber compositions.

Of course, the invention applies equally well to those cases in which a coloured reinforcing filler is selected which is compatible with the colour desired for the tyre, this coloured filler possibly being a naturally coloured filler, or alternatively obtained by a prior colouring operation, for example a precoloured silica or alumina.

The silica used may be any reinforcing silica known to the person skilled in the art, in particular any precipitated or pyrogenic silica having a BET surface area and a specific CTAB surface area both of which are less than 450 m^2/g, even if the highly dispersible precipitated silicas are preferred, in particular when the invention relates to tyres having a low rolling resistance. "Highly dispersible silica" is understood to mean any silica having a very substantial ability to disagglomerate and to disperse in a polymer matrix, which can be observed in known manner by electron or optical microscopy on thin sections. As non-limitative examples of such preferred highly dispersible silicas, mention may be made of the silica Perkasil KS 430 from Akzo, the silica BV 3380 from Degussa, the silicas Zeosil 1165 MP and 1115 MP from Rhône-Poulenc, the silica Hi-Sil 2000 from PPG, the silicas Zeopol 8741 or 8745 from Huber, and treated precipitated silicas such as, for example, the aluminium-"doped" silicas described in application EP-A-0 735 088.

The reinforcing alumina preferably used is a highly dispersible alumina having a BET surface area from 30 to 400 m^2/g, more preferably 80 to 250 m^2/g, an average particle size of at most 500 nm, more preferably at most 200 nm, a high amount of reactive Al-OH surface functions, as described in application EP-A-0 810 258 referred to above. Non-limitative examples of such reinforcing aluminas are in particular the aluminas A125, CR125 and D65CR of Baïkowski.

The physical state in which the reinforcing white filler is present is immaterial, whether it be present in the form of a powder, microbeads, granules or balls. Of course, "reinforcing white filler" is also generally understood to mean mixtures of different reinforcing

white fillers, in particular highly dispersible silicas and/or aluminas such as described above.

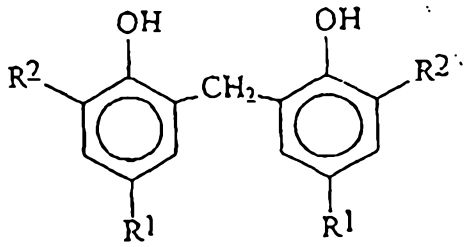
Any known coupling agent can be used to produce the bond between the reinforcing white filler and the diene elastomer, such as organosilanes, in particular polysulphurised alkoxysilanes such as bis(trialkoxy-(C_1-C_4)silylpropyl) tetrasulphides, in particular bis(trimethoxysilylpropyl) or bis(triethoxysilylpropyl) tetrasulphides, in particular the latter of these compounds, of formula $[(C_2H_5O)_3Si(CH_2)_3S_2]_2$, sold, for example, by Degussa under the name Si69, or by Osi under the name URC2.

II-3. Anti-photo-oxidising system

As stated above, the tyre composition according to the invention is protected against photo-oxidising ageing by an anti-photo-oxidising system which is light-fast and non-staining with respect to this composition, based on at least:

(A) a 2,2'-methylene-bis-[4-(C_1 to C_{10})alkyl-6-(C_1 to C_{12})alkylphenol];
(B) a dialkyl thiodipropionate, the alkyl radicals of which, which may be identical or different, are C_1 to C_{30} radicals, preferably C_8 to C_{20} radicals;
(C) a 2-(2-hydroxyphenyl)benzotriazole;
(D) an "HALS" amine derived from 2,2,6,6-tetramethyl piperidine.

The phenolic compounds A are known antioxidants. Preferred compounds A are those of the following general formula (I)

(I) 

in which

R^1 = C_1 to C_4 alkyl, preferably methyl or ethyl,

R^2 = C_1 to C_6 alkyl, or C_5 to C_{12} cycloalkyl.

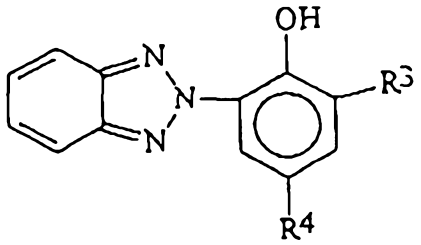
Preferably compound A is a 2,2'-methylene-bis-[4-(methyl or ethyl)-6-(C_1-C_4)alkylphenol] or a 2,2'-methylene-bis-[4-(methyl or ethyl)-6-(C_7-C_8)cycloalkylphenol].

Compound A is advantageously selected from the group formed by 2,2'-methylene-bis-[4-methyl-6-t-butylphenol], 2,2'-methylene-bis-[4-ethyl-6-t-butylphenol], 2,2'-methylene-bis-[4-methyl-6-cyclohexylphenol], 2,2'-methylene-bis-[4-methyl-6-alpha-methyl-cyclohexylphenol] or 2,2'-methylene-bis-[4-methyl-6-nonylphenol]. More preferably still, the compound A selected is 2,2'-methylene-bis-[4-(methyl)-6-t-butylphenol].

Dialkyl thiodipropionates (alkyl-O-CO-CH_2-CH_2-S-CH_2-CH_2-CO-O-alkyl) are also known antioxidants. As preferred compounds B, mention will be made in particular of those whose two alkyl radicals are identical C_8-C_{20} radicals, advantageously dilauryl(C_{12})-thiodipropionate, or distearyl(C_{18})-thiodipropionate (or dioctadecyl-2,2'-thiodipropionate).

Compound C is a UV absorber ("UVA") of the known family of the 2-(2-hydroxyphenyl)benzotriazoles, which is preferably in accordance with the following general formula (II):

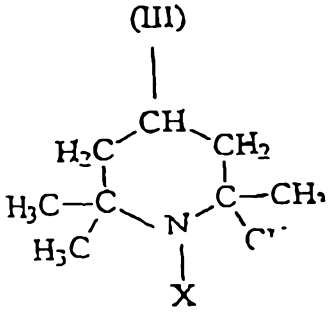
(II)



in which R^3 and R^4, which may be identical or different, represent various substituted or non-substituted, straight-chain or branched hydrocarbon radicals, in particular C_1 to C_4 alkyls, in particular methyl or ethyl, or C_7 to C_{20} alkylaryls. The benzotriazole ring may itself be substituted in the position 4, for example halogenated, in particular chlorinated.

Compound D is a "HALS" amine ("Hindered Amine Light Stabilizers") derived from 2,2,6,6-tetramethyl-piperidine, which is preferably in accordance with the general formula (III) below (with X preferably selected from hydrogen or a hydrocarbon group comprising 1 to 20 carbon atoms, for example a C_1-C_{20} alkoxyl):

(III)



Such HALS amines may be polymeric, and may have a very large variety of substituents in the position 4; they are well-known in the field of UV stabilisers and have been described in a large number of documents, for example in *"Polymer Stabilization and Degradation"*, ACS symposium series 280, Ed. P.P. Klemchuk (1985).

The anti-photo-oxidising system as described above has proved sufficiently effective by itself for anti-photo-oxidising protection of the tyre compositions according to the invention; it may therefore advantageously constitute the sole anti-photo-oxidising system, that is to say, both anti-(thermo-)oxidising and anti-UV, present in the compositions according to the invention.

Depending on the intended applications and the nature of the diene elastomer to be protected, compounds A, B, C and D are present in the compositions according to the invention in the following preferred amounts (in phr):

A: 1 to 5, more preferably 1.5 to 2.5;
B: 0.5 to 3, more preferably 0.5 to 1.5;
C: 0.5 to 3, more preferably 0.5 to 1.5;
D: 0.5 to 3, more preferably 0.5 to 1.5,

the total content of the anti-photo-oxidising system (A+B+C+D) preferably being within a range from 2.5 to 10 phr, more preferably from 3.0 to 7.0 phr.

Below the minimum amounts indicated, the effect of the system may be insufficient, whereas beyond the maximum amounts indicated no further improvement in the protection is observed, whilst the costs of the formulation continue to increase.

II-4. Colouring agent

To implement the invention, any type of colouring agent known to the person skilled in the art may be used, this colouring agent possibly being organic or inorganic, and soluble or insoluble in the compositions according to the invention. By way of example, mention may be made of mineral colouring agents such as, for example, powdered metals, in particular powdered copper or aluminium, or various metal oxides, in particular silicates, aluminates, titanates, iron oxides or hydroxides, or mixed oxides of different metallic elements such as Co, Ni, Al or Zn. Mention may also be made of organic pigments such as indanthrones, diketo-pyrrolo-pyrroles or diazo condensates, and organometallic pigments such as phthalocyanines.

The colour of the compositions according to the invention may thus vary to a very large extent, by way of example different shades of red, orange, green, yellow, blue or even brown or grey. Equally, no colouring agent may be used, and it may be decided to retain the original colour of the reinforcing filler, be it white or coloured.

II-5. Various additives

Of course, the compositions according to the invention contain, in addition to the compounds previously described, all or part of the constituents usually used in diene rubber compositions for tyres, such as plasticisers, a cross-linking system based either on sulphur or on sulphur donors, vulcanisation accelerators, extender oils, of the aromatic, naphthenic or paraffinic type, other non-staining antidegradants, in particular antiozonant waxes and

chemically active antiozonants, in particular cyclic acetals, or also various anti-fatigue agents.

The compositions according to the invention may contain coupling agents and/or covering agents for the reinforcing filler which are other than those mentioned above, in combination with or instead of the latter, such as polyols, amines or alkoxysilanes.

III. EXAMPLES OF EMBODIMENT OF THE INVENTION

In the following examples, the rubber compositions are prepared by processing the diene elastomers according to entirely known techniques, by thermomechanical working in a internal paddle mixer followed by mixing on an external mixer.

By way of example, the procedure is as follows: the elastomer or the mixture of elastomers is introduced into an internal mixer, filled to 70%, the temperature of which is about 60°C, then after a suitable kneading time, for example of the order of 1 minute, all the other ingredients are added with the exception of the vulcanisation system; the thermomechanical kneading work is continued until a dropping temperature of 175°C; the mixture thus obtained is recovered then the vulcanisation system is added on an external mixer (homo-finisher) at 30°C. The vulcanisation is effected at 150°C for 45 minutes.

In this test, seven red rubber compositions intended for the manufacture of tyre treads are compared.

These compositions are identical, except for the anti-photo-oxidising protection system, which is absent in the case of composition No. 1 (non-protected control), based on a PPD-type antioxidant for composition No. 2 (reference composition), and based on different associations involving all or some of compounds A to D for the other compositions.

Composition No. 7 is the only composition according to the invention, comprising the 4 compounds (A+B+C+D).

The compounds A to D used, which are all commercially available, are as follows:

(A): 2,2'-methylene-bis-(4-methyl-6-t-butylphenol];
(B): distearyl thiodipropionate;
(C): 2-(2-hydroxyphenyl)benzotriazole in accordance with formula (II) in which:
- R^3 = t-butyl;
- R^4 = CH_2-CH_2-CO-O-[$(CH_2)_2$-O]$_n$-H;

(D) tertiary "HALS" amine derived from 2,2,6,6-tetramethyl piperidine in accordance with formula (III) in which:
- substituent in position 1 (X): O-C_8H_{17} (capryloxyl),
- substituent in position 4: [O-CO-$(CH_2)_4$]$_2$.

The diene elastomer is an SBR/BR blend. The SBR elastomer (styrene-butadiene copolymer) is prepared in solution, and comprises 25.6% styrene, 60% 1-2-polybutadiene units and 23% trans-1-4 polybutadiene units. The BR elastomer (polybutadiene) is a commercial product, comprising more than 90% cis-1,4 bonds (about 98%).

Tables 1 to 3 show in succession the formulation of the various compositions (Table 1 - amounts of the different products in phr), their properties after curing and the evolution of their mechanical properties after thermo-oxidation and after photo-oxidation (Table 2), and finally the evolution of their colorimetric properties after photo-oxidation (Table 3).

On reading these different tables of results, the following can be noted:

- the conventional rubber properties (Table 2), after curing and before ageing, are little

different from one composition to the other, whether they be protected by one or more antidegradants or not;

- after thermo-oxidation (Table 2), it is noted that the results obtained on the composition according to the invention (No. 7) are those which are closest to the results obtained with the conventional antioxidant (6-PPD) acting as a reference. It should be noted here that the lowest percentages of evolution of M10 and M100, noted on the non-protected control (Composition No. 1) are not indicative here of a lower degree of degradation; on the contrary, associated with hysteresis losses which do not decrease, these low percentages of evolution are linked in a manner known to the person skilled in the art to degradation by splitting of the elastomeric chains, on the control composition;

- after photo-oxidation (Table 2), it is noted again that the best results are obtained by the anti-photo-oxidising system combining the four compounds A, B, C and D (composition No. 7); these results are comparable to those obtained on the reference composition No. 2: see evolution of the Shore A hardness, of F10 and more particularly of F25;

- finally, with regard to the evolution of the colorimetric properties (Table 3), it is noted that composition No. 2, which is protected by the PPD derivative, is degraded very substantially and in crippling manner (pronounced blackening), whereas composition No. 7 according to the invention on the other hand shows excellent colour stability (no staining visible), virtually

equivalent to that recorded on the control composition devoid of antidegradant; the parameter ΔE is close to 10 for the composition according to the invention, whereas it is greater than 30 for the composition based on PPD derivative.

This test clearly shows that compounds A to D, in composition No. 7 according to the invention, reciprocally reinforce their effects, thus making it possible to obtain a far better compromise in terms of properties after ageing than for the other compositions.

Finally, running tests of long duration were performed on passenger cars with numerous coloured tyres according to the invention (dimensions 155/70 SR 13; 175/70 SR 13; 185/65 HR 14); these tyres had treads and/or sidewalls coloured in different colours (red, yellow or green).

These rolling tests led to the following results:

- endurance properties equivalent to those observed on conventional black compositions, filled at least in part with carbon black;

- adhesion performance, in particular on wet ground, and rolling resistance performance better than those obtained with conventional compositions filled with carbon black, these performances being as good as those obtained on silica-based compositions such as described in the aforementioned application EP-A-0 501 227;

- no degradation of the colours after travelling for several tens of thousands of kilometres.

In conclusion, the compositions according to the invention, owing to a synergistic combination of four specific compounds, impart to coloured tyres very good resistance to atmospheric ageing due to the combined action of oxygen and UV light, this resistance being comparable to that obtained using a derivative of the PPD type, while guaranteeing these tyres excellent colour stability which would be impossible with a conventional 6-PPD-type antidegradant.

Table 1

Composition No.	1	2	3	4	5	6	7
SBR (1)	50	50	50	50	50	50	50
BR (2)	50	50	50	50	50	50	50
Silica (3)	80	80	80	80	80	80	80
Natural kaolin	5	5	5	5	5	5	5
Coupling agent (4)	6.4	6.4	6.4	6.4	6.4	6.4	6.4
Paraffin oil	25	25	25	25	25	25	25
ZnO	2.5	2.5	2.5	2.5	2.5	2.5	2.5
6-PPD (5)		1.5					
Compound A (6)			2	2	2	2	2
Compound B (7)				1	1	1	1
Compound C (8)					1		1
Compound D (9)						1	1
Wax (10)	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Colouring agent (11)	2	2	2	2	2	2	2
Stearic acid	2	2	2	2	2	2	2
Sulphur	1.1	1.1	1.1	1.1	1.1	1.1	1.1
CBS (12)	2	2	2	2	2	2	2
DPG (13)	1.5	1.5	1.5	1.5	1.5	1.5	1.5

(1) butadiene-styrene copolymer
(2) polybutadiene Europrene Cis (from Enichem)
(3) silica Zeosil 1165MP (from Rhône-Poulenc)
(4) Si69 (from Degussa)
(5) N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine
(6) 2,2'-methylene-bis(4-methyl-6-t-butylphenol) (Vulkanox BKF, from Bayer)
(7) dioctadecyl-2,2-thiodipropionate (Irganox PS 802, from Ciba-Geigy)
(8) 2-(2-hydroxyphenyl)benzotriazole (UVA Tinuvin 213, from Ciba-Geigy)
(9) HALS amine derived from 2,2,6,6-tetramethylpiperidine (Tinuvin 123, from Ciba-Geigy)
(10) antiozonant wax (Redezon 500, from Repsol)
(11) pigment Cromophtal Red BRN CI - Red 144 (from Ciba-Geigy)
(12) N-cyclohexyl-benzothiazyl-sulphenamide
(13) 1,3-diphenylguanidine

Table 2

Composition No.	1	2	3	4	5	6	7
Before thermo-oxidation:							
M10 (MPa)	5	5.1	4.9	5.4	5.2	5.3	5.4
M100 (MPa)	2	2.1	2	2.1	2	2.2	2.2
Shore A hardness	65	65	66	68	66	66	66
HL60	31	30	31	32	32	32	32
After thermo-oxidation (30 days at 70°C):							
M10 (MPa)	5.5	5.9	6.2	6.3	6.2	6.3	6.2
% evolution	10	16	27	17	19	19	15
M100 (MPa)	2.5	2.8	2.8	2.8	2.7	3.0	2.9
% evolution	25	33	40	33	35	36	32
HL	33	26	28	27	27	28	27
Before photo-oxidation:							
F10 (MPa)	0.55	0.59	0.58	0.6	0.6	0.62	0.55
F25 (MPa)	0.85	0.88	0.86	0.9	0.87	0.88	0.79
After photo-oxidation (12 days):							
F10 (MPa)	0.95	0.95	0.97	1.02	0.99	1.03	0.9
% evolution	72	61	67	70	65	66	64
F25 (MPa)	1.45	1.37	1.44	1.48	1.42	1.42	1.23
% evolution	71	56	67	64	63	61	56
Shore A hardness	78	76.8	78.5	81	77.8	78.5	76
% evolution	20	18	19	19	18	19	17

Table 3

Composition No.	1	2	7
Initial colorimetric properties:			
L*	+38	+34	+35
a*	+36	+31	+34
b*	+22	+18	+20
After 12 days' photo-oxidation:			
ΔL	-5	-14	-5
Δa*	-5	-28	-8
Δb*	-2	-14	-5
ΔE	+7	+34	+11

CLAIMS

1. A white, clear or coloured tyre rubber composition devoid of carbon black, including at least one diene elastomer, a white or coloured reinforcing filler and an anti-photo-oxidising protection system, characterised in that said protection system is based on at least:

(A) a 2,2'-methylene-bis-[4-(C_1 to C_{10})alkyl-6-(C_1 to C_{12})alkylphenol];
(B) a dialkyl thiodipropionate, the alkyl radicals of which, which may be identical or different, are C_1 to C_{30} radicals, preferably C_8 to C_{20} radicals;
(C) a 2-(2-hydroxyphenyl)benzotriazole;
(D) an "HALS" amine derived from 2,2,6,6-tetramethyl piperidine.

2. A composition according to Claim 1, in which compound A is a 2,2'-methylene-bis-[4-(C_1-C_4)alkyl-6-(C_1-C_7)alkyl phenol].

3. A composition according to Claim 2, in which compound A is 2,2'-methylene-bis-[4-(methyl)-6-t-butylphenol].

4. A composition according to any one of Claims 1 to 3, in which compound B is a (C_8 to C_{20})dialkyl thiodipropionate.

5. A composition according to Claim 4, in which compound B is dilauryl thiodipropionate or distearyl thiodipropionate.

6. A composition according to any one of Claims 1 to 5, in which the diene elastomer is selected from the group which consists of polybutadienes, polyisoprenes

12. A composition according to any one of claims 9 to 11, in which titanium oxide is associated with the silica and/or alumina.

13. A composition according to claim 12, wherein said titanium oxide is in an amount of 0.5 to 7% (% by weight relative to the weight of silica and/or alumina).

14. A coloured tyre or rubber article for such a tyre, characterised in that it includes a rubber composition according to any one of claims 1 to 13.

15. A rubber article according to claim 14, selected from the group consisting of treads, underlayers, sidewalls, protectors and beads.

16. A process for protecting against photo-oxidising ageing a white, clear or coloured tyre rubber composition devoid of carbon black, characterised in that there is incorporated by mixing into said composition before the vulcanisation thereof an anti-photo-oxidising system based on at least:

(A) a 2,2'-methylene-bis-[4-(C_1 to C_{10})alkyl-6-(C_1 to C_{12})alkylphenol];
(B) a dialkyl thiodipropionate, the alkyl radicals of which, which may be identical or different, are C_1 to C_{30} radicals;
(C) a 2-(2-hydroxyphenyl)benzotriazole;
(D) an "HALS" amine derived from 2,2,6,6-tetramethyl piperidine.

17. A process according to claim 16, wherein the said alkyl radicals are C_8 to C_{20} in radicals.

18. A process according to claim 16 or 17, in which compound A is a 2,2'-methylene-bis-[4-(C_1-C_4) alkyl-6-(C_1-C_7)-alkylphenol].

19. A process according to claim 18, in which compound A is 2,2'-methylene-bis-[4- (methyl) -6-t-butylphenol].

20. A process according to any one of claims 16 to 19, in which compound B is a (C_8 to C_{20}) dialkyl thiodipropionate.

21. A process according to claim 20, in which compound B is dilauryl thiodipropionate or distearyl thiodipropionate.

22. The use, for protecting against photo-oxidation of white, clear or coloured tyre rubber compositions devoid of carbon black, of an anti-photo-oxidising protection system based on at least:

(A) a 2,2'-methylene-bis-[4-(C_1 to C_{10})alkyl-6-(C_1 to C_{12})alkylphenol];
(B) a dialkyl thiodipropionate, the alkyl radicals of which, which may be identical or different, are C_1 to C_{30} radicals;
(C) a 2-(2-hydroxyphenyl)benzotriazole;
(D) an "HALS" amine derived from 2,2,6,6-tetramethyl piperidine.

23. A process according to claim 22, wherein the said alkyl radicals are C_8 to C_{20} radicals.

24. The use according to claim 22 or 23, in which compound A is a 2,2'-methylene-bis-[4-(C_1 to C_4)alkyl-6-(C_1 to C_7)alkylphenol].

or natural rubber, butadiene-styrene copolymers, butadiene-isoprene copolymers, isoprene-styrene copolymers, butadiene-styrene-isoprene copolymers, or a mixture of two or more of these compounds.

7. A composition according to claim 6, in which the diene elastomer is a butadiene-styrene copolymer prepared in solution having a styrene content of between 20% and 30% by weight, a content of vinyl bonds of the butadiene part of between 15% and 65%, a content of trans-1, 4 bonds of between 15% and 75%, and a glass transition temperature of between -20°C and -55°C.

8. A composition according to claim 7, wherein the said butadiene-styrene copolymer is used in a mixture with a polybutadiene having preferably more than 90% cis-1, 4 bonds.

9. A composition according to any one of claims 1 to 8, in which the reinforcing filler is formed majoritarily of silica and/or alumina.

10. A composition according to claim 9, in which another white filler selected from chalk, talc or kaolin is associated with the silica and/or alumina.

11. A composition according to claim 10, wherein said other white filler is in an amount of 2.5 to 12.5% (% by weight relative to the weight of silica and/or alumina).

25. The use according to claim 24, in which compound A is 2,2'-methylene-bis-[4- (methyl) -6-t-butylphenol].

26. The use according to any one of claims 22 to 25, in which compound B is a (C_8 to C_{20})dialkyl thiodipropionate.

27. The use according to claim 26, in which compound B is dilauryl thiodipropionate or distearyl thiodipropionate.

DATED this 12th day of March 2002

COMPAGNIE GENERALE DES ETABLISSEMENTS MICHELIN - MICHELIN & CIE

WATERMARK PATENT & TRADE MARK ATTORNEYS
290 BURWOOD ROAD
HAWTHORN VICTORIA 3122
AUSTRALIA

P16672AU00 SKP/DHS/PCP