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A tyre, the sidewalls of which comprise a vulcanised rubber composition

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Title: A tyre, the sidewalls of which comprise a vulcanised rubber composition.

ABSTRACT

The present invention relates to a tyre the sidewalls of which comprise a vulcanised rubber composition. Said composition comprises, in a quantity comprised between 0.5 phr and 10 phr (weight parts per hundred parts of rubber), at least one polymer which comprises an oxy group defined by the -O- formula and, linked to the one side of said oxy group, at least one polyoxyalkylene block according to the $(C_nH_{2n}O)_x$ formula,

where n is equal to 2 or 3 and x is either equal to 2 or 15 or comprised therebetween,

said at least block being linked to an hydrogen atom at the chain end, so that said hydrogen atom forms an alcohol function with the terminal oxygen atom of said at least block.

According to the invention, said at least polymer comprises, linked to the other side of said oxy group, an aliphatic part which belongs to the group consisting of

- a blend of aliphatic alkyl chains whose number of carbon atoms is in average either substantially equal to 10 or 14, or comprised therebetween, and

-an aliphatic chain which comprises an alkyl chain whose number of carbon atoms is equal to 13.

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Invention Title: A TYRE, THE SIDEWALLS OF WHICH COMPRISE A VULCANISED RUBBER COMPOSITION

The following statement is a full description of this invention, including the best method of performing it known to :- us

SPECIFICATION

BACKGROUND OF THE INVENTION

The present invention relates to a tire including sidewalls which comprise a vulcanized rubber composition based on at least one elastomer. The invention particularly applies to the protection of said tire against the effects of migrations of antioxidants and antiozonants compounds incorporated in said sidewalls, which effects can be seen on the outer faces of said sidewalls.

It is known that certain rubber compositions are very sensitive to the action of ozone. It is particularly the case of vulcanized rubber compositions based on dienic elastomers.

When an article made with such a vulcanized elastomer composition is subjected to the action of prolonged static and dynamic stresses in the presence of ozone, some more or less marked cracks which can be seen on the surface of the article appear. These cracks are oriented perpendicularly to the direction of the stress, and their growing under the effect of said remaining stress may cause complete failure of the article.

In order to minimize these effects of ozone, antiozone compounds, which are designed to slow down the formation and propagation of the cracks under static and dynamic stressing conditions, are commonly incorporated into these articles and, particularly, into the sidewalls based on elastomers that are included in tires, as well as waxes, which are designed to provide additional static protection by forming a protective surface coating on the surface of the sidewalls.

The association of these antiozone compounds and of these waxes has proved its effectiveness for the minimization of cracks at the surface of the sidewalls.

Unfortunately, the most effective antiozone compounds are also characterized by a very high tendency to migrate through their polymeric substrate and end up staining and coloring the surfaces that are adjacent to said substrate. More precisely, yellowish or brown stains appear at the surface of the sidewalls. This phenomenon is called « coloration ».

The Japanese Patent Document JP-A-5 194790 discloses, in a rubber composition for the sidewalls of a tire comprising at least one elastomer, the use of several specific polymeric

surfactants of the polyoxyethylene ether type, in order to cope with that « coloration » phenomenon. Those particular surfactants are characterized by a hydrophilic-lipophilic balance (HLB) which is comprised between 10.7 and 15.0, and they are made of polyoxyethylene nonylphenylether, polyoxyethylene stearylether, or polyoxyethylene oleylether.

SUMMARY OF THE INVENTION

The purpose of the present invention is to provide a tire including sidewalls which comprise a new vulcanized rubber composition based on at least one elastomer, said tire allowing to meet the drawbacks produced by said deleterious phenomenon.

For this purpose, a tire according to the invention is such that said rubber composition comprises, in a quantity comprised between 0.5 phr and 10 phr, (weight parts per hundred parts of rubber), at least one polymer which comprises an oxy group defined by the -O- formula and, linked to the one side of said oxy group, at least one polyoxyalkylene block according to the $(C_nH_{2n}O)_x$ formula,

where n is an integer number that is either equal to 2 or 3,

where x is an integer or decimal number that is either equal to 2 or 15 or comprised therebetween,

said at least block being linked to an hydrogen atom which is located at the chain end of said at least polymer, in such a manner that said hydrogen atom forms an alcohol function with the terminal oxygen atom of said at least block,

and the inventors have unexpectedly found that said drawbacks can be greatly met by using, for said at least polymer, a polymer that comprises, linked to the other side of said oxy group, a specific aliphatic part which belongs to the group consisting of

- a blend of aliphatic alkyl chains whose number of carbon atoms is in average either substantially equal to 10 or 14, or comprised therebetween, and
- an aliphatic alkyl chain whose number of carbon atoms is equal to 13.

It is to be noted that such a novel and unexpected specific selection for said aliphatic part provides a uniform black appearance for the sidewalls of the corresponding tires according

to the invention, which is durable and therefore significantly enhances the aesthetic appearance of the latter.

According to a first example of the invention, said aliphatic part is a blend of aliphatic alkyl chains whose number of carbon atoms is in average either substantially equal to 10 or to 14, or comprised therebetween.

Advantageously, said number of carbon atoms is in average substantially equal to 14, said at least block consisting in a sole polyoxyethylene block whose number x is equal to 4. Then, the hydrophilic-lipophilic balance (HLB) of said polymer is substantially equal to 9.1.

One should note in this case that such a specific selection for the aliphatic part not only provides a black color for the whole outer surface of the sidewalls, but also a glossy appearance for said surface which further enhances the sidewalls.

Also advantageously, said number of carbon atoms is in average substantially equal to 14, said at least block consisting in

-a polyoxypropylene block whose number x is equal to 5, and

- a polyoxyethylene block whose number x is equal to 4.

Then, the HLB of said polymer is substantially equal to 9.5.

Again in this particular case, a glossy black color is obtained for the sidewalls.

Also advantageously, said number of carbon atoms is in average substantially equal to 12, said at least block consisting in a sole polyoxyethylene block whose number x is equal to 7.

Then, the HLB of said polymer is substantially equal to 12.6.

Again in this particular case, a glossy black color is obtained for the sidewalls.

Also advantageously, said number of carbon atoms is in average substantially equal to 14, said at least block consisting in a sole polyoxyethylene block whose number x is equal to 2.

Then, the HLB of said polymer is substantially equal to 5.9.

Again in this particular case, a glossy black color is obtained for the sidewalls.

Also advantageously, said number of carbon atoms is in average substantially equal to 10, said at least block consisting in a sole polyoxyethylene block whose number x is equal to 2.5.

Then, the HLB of said polymer is substantially equal to 8.2.

Again in this particular case, a glossy black color is obtained for the sidewalls.

According to a second example of the invention, said aliphatic part which is linked to said oxy group consists in a tridecyl group, said at least block consisting in a sole polyoxyethylene block whose number x is equal to 3.

Then, the HLB of said polymer is substantially equal to to 8.6.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Several tires have been manufactured, each of them including sidewalls with a determined vulcanized rubber composition according to the invention, in comparison with a « witness » tire including sidewalls with a usual vulcanized rubber composition.

All the rubber compositions that have been tested are detailed in the following Table I (witness composition and compositions 1 to 8 according to the invention), the quantity of every compound in each composition being expressed in phr therein (weight parts per hundred parts or rubber, said rubber corresponding to butadiene rubber and natural rubber in these preferred embodiments).

In Table I,

- ▷ said carbon black is a conventional carcasse grade carbon black,
- ▷ said wax is an antiozone wax,
- ▷ said aromatic oil is a heavy oil,
- ▷ « DMBPPD » represents the N-(1,3-dimethyl butyl)-N'-phenyl-p-phenylenediamine, antioxygen and antiozone compound,
- ▷ « CBS » represents the N-cyclohexyl-benzothiazyl-sulfenamide, a vulcanization accelerator.

Moreover, each rubber composition referred to in Table I conventionally contains an antioxygen compound, such as « TMQ » (which stands for trimethylquinoline, a polymerized 1,2-dihydro-2,2,4-trimethylquinone).

▷ Synperonic A4 is the trade name of a surfactant sold by UNIQEMA, whose HLB is substantially equal to 9.1, which is made up of a polymer comprising, linked to the one side and to the other side of an oxy radical of formula -O-, respectively a blend R of alkyl groups and one block of polyoxyethylene, according to the formula

$R\text{-}O\text{-}(C_2H_4O)_4\text{-}H$,

where said alkyl groups are acyclic ones that comprise from 13 to 15 atoms of carbon (14 in average).

More precisely, said polyoxyethylene block is linked to an hydrogen atom which is located at a chain end of this polymer, in such a manner that said hydrogen atom forms an alcohol function with the terminal oxygen atom of said polyoxyethylene block.

▷ Synperonic LF/RA 280 is the trade name of a surfactant sold by UNIQEMA, whose HLB is substantially equal to 9.5, which is made up of a polymer comprising, linked to the one side and to the other side of an oxy radical -O-, respectively a blend R of alkyl groups and two blocks polyoxyethylene and polyoxypropylene, according to the formula

$R\text{-}O\text{-}(C_3H_6O)_5\text{-}(C_2H_4O)_4\text{-}H$,

where said alkyl groups comprise from 13 to 15 carbon atoms (14 in average), and where the hydrogen atom at the chain end of the polymer also forms an alcohol function with the terminal oxygen atom of said polyoxyethylene block.

▷ Synperonic L7 is the trade name of a surfactant sold by UNIQEMA, whose HLB is substantially equal to 12.6, which is made up of a polymer comprising, linked to the one side and to the other side of an oxy radical -O-, respectively a blend R of alkyl groups and one block of polyoxyethylene, according to the formula

$R\text{-}O\text{-}(C_2H_4O)_7\text{-}H$,

where said alkyl groups comprise an average number of carbon atoms that is substantially equal to 12, and where the hydrogen atom at the chain end of the polymer also forms an alcohol function with the terminal oxygen atom of said polyoxyethylene block.

▷ Synperonic A2 is the trade name of a surfactant sold by UNIQEMA, whose HLB is substantially equal to 5.9, which is made up of a polymer comprising, linked to the one side and to the other side of an oxy radical -O-, respectively a blend R of alkyl groups and one block of polyoxyethylene, according to the formula

$R\text{-}O\text{-}(C_2H_4O)_2\text{-}H$,

where said alkyl groups comprise an average number of carbon atoms that is substantially equal to 14, and where the atom of hydrogen at the chain end of the polymer also forms an alcohol function with the terminal oxygen atom of said polyoxyethylene block.

▷ Synperonic 91/2.5 is the trade name of a surfactant sold by UNIQEMA, whose HLB is substantially equal to 8.2, which is made up of a polymer comprising, linked to the one side and to the other side of an oxy radical -O-, respectively a blend R of alkyl groups and one block of polyoxyethylene, according to the formula

$R\text{-}O\text{-}(C_2H_4O)_{2.5}\text{-}H$,

where said alkyl groups comprise between 9 and 11 atoms of carbon, and where the hydrogen atom at the chain end of the polymer also forms an alcohol function with the terminal oxygen atom of said polyoxyethylene block.

▷ Synperonic 13/3 is the trade name of a surfactant sold by UNIQEMA, whose HLB is substantially equal to 8.6, which is made up of a polymer comprising, linked to the one side and to the other side of an oxy radical -O-, respectively a tridecyl group and one block of polyoxyethylene, according to the formula

$C_{13}H_{27}\text{-}O\text{-}(C_2H_4O)_3\text{-}H$,

where the hydrogen atom at the chain end of the polymer also forms an alcohol function with the terminal oxygen atom of said polyoxyethylene block.

TABLE I

Compounds	«witness»	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	Comp. 6	Comp. 7	Comp. 8
butadiene rubber	65	65	65	65	65	65	65	65	65
natural rubber	35	35	35	35	35	35	35	35	35
carbon black	60	60	60	60	60	60	60	60	60
wax	1	1	1	1	1	1	1	1	1
stearic acid	1	1	1	1	1	1	1	1	1
ZnO	3	3	3	3	3	3	3	3	3
DMBPPD	3	3	3	3	3	3	3	3	3
aromatic oil	21	21	21	21	21	21	21	21	21
S	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
CBS	1	1	1	1	1	1	1	1	1
Synperonic A4		2	3						
Synperonic LF/RA 280				2	3				
Synperonic L7						2			
Synperonic A2							2		
Synperonic 91/2.5								2	
Synperonic 13/3									2

Each tire whose sidewalls include one of said rubber compositions according to the invention has been tested, in order to determine the following properties:

- The plasticity and scorch values (t5) have been measured according to ASTM D1646.
- The Shore A Hardness values have been measured according to ASTM D2240, with a device whose name is « Durometer of type A ».
- The M300 values have been measured according to ASTM D412, Test Method A.

- The severity of cracking and the coloration phenomenon after ozone static rubber test "S18" (called « Stat. Test » in Table II):

This S18 test has been carried out according to ASTM D1149, the samples dimensions excepted. Each sample is here a 20 x 145 mm one, in place of a 10 x 100 +/- 25 mm one that is specified in ASTM D1149.

Said samples, which respectively contain said witness composition and said compositions 1 to 8 according to the invention, hang on a rod for 2 days in the laboratory (under normal atmosphere) and then in an ozone chamber for 14 days (the ozone concentration in said chamber is 50 pphm at 38° C).

a) The severity of cracking has then been evaluated for each sample, by subjectively using three parameters a/ b/ c :

the number a, width b, and depth of cracks c, which values can vary within a scale ranging from 0 to 5 (the higher each value, the greater the number, the width and the depth for the cracks).

b) The coloration phenomenon of each sample has also been evaluated in the end of this static test, by means of a subjective rating system.

Said subjective rating system consists in an appearance rate (« appear. rate » in Table II), which can vary from 0 to 4.

More precisely, the possible values of said appearance rate respectively correspond to the following appearances:

4 is glossy black, 3 is black, 2 is matte black, 1 is lightly colored and 0 is colored.

The color of each sample in the end of said static test has also been reported in Table II.

- Coloration after a specific ozone dynamic rubber test (called « Dyn. Test » in Table II):

Said specific dynamic test is derived from the Standard D25 Test which is carried out according to ASTM D3395, namely with an ozone concentration of 50 pphm at 38° C that is specified therein.

Each sample is also a 20 x 145 mm one, in place of a 10 x 100 +/- 25 mm one that is specified in ASTM D3395.

However, whereas the Standard D25 Test is designed to evaluate the severity of cracking, the specific dynamic test that has been run here has particularly been used to evaluate in the end of it the coloration phenomenon of each sample, by means of the above-referred subjective rating system.

In fact, said specific dynamic test also differs from the Standard D25 Test, in that each sample is run for approximately 10 days, namely 1.5 week instead of the 2 days specified in ASTM D3395.

The color of each sample in the end of said specific dynamic test has also been reported in Table II, as for said static test.

TABLE II

	Witness	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	Comp. 6	Comp. 7	Comp. 8
Plasticity	45	49	43	49	45	48	51	51	50
Shore	55	57	57	58	55	57	58	57	58
M300	6.8	7.3	7.4	7.5	6.8	7.2	7.1	7.1	7.9
Scorch	20	16	15	18	17	15	17	17	18
Stat. Test									
Cracking	2/1/1	0/0/0	0/0/0	0/0/0	0/0/0	0/0/0	0/0/0	0/0/0	0/0/0
Appear. Rate	2	3	3	3	4	3	4	4	-
color	matte black	black	black	black	glossy black	black	glossy black	glossy black	-
Dyn.Test									
Appear. rate	0	3	4	3	3	4	2	2	2
color	brown	black	glossy black	black	black	glossy black	matte black	matte black	matte black

Table II shows that after being exposed in a static or dynamic way to an ozone atmosphere and in comparison with the « witness », a sample which comprises any of the vulcanized rubber compositions according to the present invention, exhibits

- no initiation of cracking under static ozone exposure,
- no coloration phenomenon (namely a black color instead of a brown one for the « witness »),
- and, more particularly for the samples including rubber compositions 2, 4, 5, 6 and 7, a glossy black surface which further improves the appearance of the corresponding tires.

Moreover, Table II shows that the samples which comprise a rubber composition according to the invention are characterized by good mechanical properties.

Besides, it has been examined whether the surface of the samples according to the invention remain intact under washing conditions.

For this purpose, said ozone dynamic Standard « D25 Test » has been run for two weeks and each sample has been washed six times intermittently during these two weeks, with various cleaners including deionized water and two commercial tire cleansers, which are sold under the trade names « Bleche-White » and « Armor All ».

After such washings, each sample comprising a vulcanized rubber composition according to the invention looked black, whereas the « witness » sample exhibited varying shades of brown, depending on the cleanser that had been used.

Moreover, each sample according to the invention showed significantly less cracking than the « witness », under all these washing conditions.

It is to be noted that the above-described examples are designed to illustrate the present invention, which means that they should not be construed as limiting its scope.

"Comprises/comprising" when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

~~WE CLAIM:~~xxxx

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A tire including sidewalls which comprise a vulcanized rubber composition based on at least one elastomer, said rubber composition comprising, in a quantity comprised between 0.5 phr and 10 phr (weight parts per hundred parts of rubber), at least one polymer which comprises an oxy group defined by the -O- formula and, linked to the one side of said oxy group, at least one polyoxyalkylene block according to the $(C_nH_{2n}O)_x$ formula,

where n is an integer number that is either equal to 2 or 3,

where x is an integer or decimal number that is either equal to 2 or 15 or comprised therebetween,

said at least block being linked to an hydrogen atom which is located at the chain end of said at least polymer, in such a manner that said hydrogen atom forms an alcohol function with the terminal oxygen atom of said at least block,

wherein said at least polymer comprises, linked to the other side of said oxy group, an aliphatic part which belongs to the group consisting of

- a blend of aliphatic alkyl chains whose number of carbon atoms is in average either substantially equal to 10 or 14, or comprised therebetween, and

-an aliphatic chain which comprises an alkyl chain whose number of carbon atoms is equal to 13.

2. A tire according to claim 1, wherein said aliphatic part is a blend of aliphatic alkyl chains whose number of carbon atoms is in average either substantially equal to 10 or to 14, or comprised therebetween.

3. A tire according to claim 2, wherein said number of carbon atoms is in average substantially equal to 14, said at least block consisting in a sole polyoxyethylene block whose number x is equal to 4.

4. A tire according to claim 3, wherein the hydrophilic-lipophilic balance (HLB) of said polymer is substantially equal to 9.1.

5. A tire according to claim 2, wherein said number of carbon atoms is in average substantially equal to 14, said at least block consisting in

-a polyoxypropylene block whose number x is equal to 5, and

- a polyoxyethylene block whose number x is equal to 4.

6. A tire according to claim 5, wherein the hydrophilic-lipophilic balance (HLB) of said polymer is substantially equal to 9.5.

7. A tire according to claim 2, wherein said number of carbon atoms is in average substantially equal to 12, said at least block consisting in a sole polyoxyethylene block whose number x is equal to 7.

8. A tire according to claim 7, wherein the hydrophilic-lipophilic balance (HLB) of said polymer is substantially equal to 12.6.

9. A tire according to claim 2, wherein said number of carbon atoms is in average substantially equal to 14, said at least block consisting in a sole polyoxyethylene block whose number x is equal to 2.

10. A tire according to claim 9, wherein the hydrophilic-lipophilic balance (HLB) of said polymer is substantially equal to 5.9.

11. A tire according to claim 2, wherein said number of carbon atoms is in average substantially equal to 10, said at least block consisting in a sole polyoxyethylene block whose number x is equal to 2.5.

12. A tire according to claim 11, wherein the hydrophilic-lipophilic balance (HLB) of said polymer is substantially equal to 8.2.

13. A tire according to claim 1, wherein aliphatic part consists in tridecyl group, said at least block consisting in a sole polyoxyethylene block whose number x is equal to 3.

14. A tire according to claim 13, wherein the hydrophilic-lipophilic balance (HLB) of said polymer is substantially equal to 8.6.

15. A tire according to any of the preceding claims, wherein said vulcanized rubber composition comprises at least one antiozone compound.

DATED this 6th day of November 2000.

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