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(71) Applicant(s)
Societe De Technologie Michelin; Michelin Recherche Et Technique S.A.

(72) Inventor(s)
Salvatore Pagano; Lucette Dumergue; Emmanuelle Pornet

(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 CA US)*: SOCIETE DE TECHNOLOGIE MICHELIN [FR/FR]; 23, rue Breschet, F–63000 Clermont–Ferrand (FR).

(71) Déposant *(pour tous les Etats désignés sauf US)*: MICHELIN RECHERCHE ET TECHNIQUE S.A. [CH/CH]; Route Louis Braille 10 et 12, CH–1763 Granges–Paccot (CH).

(72) Inventeurs; et
(75) Inventeurs/Déposants *(US seulement)*: PAGANO, Salvatore [FR/FR]; 34, boulevard Charcot, F–63100 Clermont–Ferrand (FR). DUMERGUE, Lucette [FR/FR]; Rue des Dômes, F–63360 St–Beauzire (FR). PORNET, Emmanuelle [FR/FR]; Bâtiment C – Résidence Valérie, 13, rue de Clermont, F–63200 Riom (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: RUBBER–BASED PRODUCT, METHOD FOR PRODUCING SAME, TYRE MADE FROM SAID PRODUCT TO REDUCE SAID TYRE ROLLING RESISTANCE

(54) Titre: PRODUIT A BASE DE CAOUTCHOUC, SON PROCEDE D'OBTENTION, PNEUMATIQUE CONSTITUE PAR CE PRODUIT ET PROCEDE POUR REDUIRE LA RESISTANCE AU ROULEMENT DE CE PNEUMATIQUE

(57) Abstract

The invention concerns a rubber–based product, comprising at least a buffer zone for trapping oxygen outside said product so as to protect from oxidation at least a sensitive zone of said product, said or each buffer zone containing a composition based on at least an elastomer comprising at least an iron (III) salt designed to activate oxidation in said composition. The invention is characterised in that said salt is an iron (III) salt of a carboxylic acid of formula $C_nH_{2n}O_2$, wherein n ranges from 2 to 5. Said product is obtained by incorporating by mechanical process said salt in said elastomer or elastomers contained in said composition, for said buffer zone. The invention is advantageously used in a tyre outer casing and provides improved rolling resistance.

(57) Abrégé

La présente invention concerne un produit à base de caoutchouc, du type comportant au moins une zone tampon prévue pour piéger l'oxygène extérieur audit produit en vue de protéger de l'oxydation au moins une zone sensible dudit produit, ladite ou chaque zone tampon contenant une composition à base d'au moins un élastomère qui comprend au moins un sel de fer (III) prévu pour activer l'oxydation dans ladite composition, caractérisé en ce que ledit sel est un sel de fer (III) d'un acide carboxylique répondant à la formule brute $C_nH_{2n}O_2$, où n peut aller de 2 à 5. Ce produit est obtenu en incorporant par travail mécanique ledit sel à l'élastomère ou aux élastomères que comprend ladite composition, pour ladite zone tampon. L'invention est avantageusement mise en oeuvre dans une enveloppe de pneumatique et confère une résistance au roulement améliorée.

TITLE: Product based on rubber, process for obtaining it, tyre made from the said product and process for reducing the rolling resistance of the said tyre.

The present invention concerns a product based on rubber, the process for obtaining it, a tyre made from the said product and a process for reducing the rolling resistance of the said tyre.

One of the main concerns of tyre manufacturers is to increase the life of the tyres. In particular, it is important to improve the endurance in relation to oxidising processes of the rubber compositions, the metallic or textile reinforcement and the interfaces between those mixes and reinforcements.

A known method of reducing these oxidation phenomena consists in restricting the amount of oxygen coming from the tyre inflation air or from the atmosphere outside the tyre, that gets to a zone of the tyre cover that is particularly sensitive to oxidation. For a very long time this has been done with a layer of butyl rubber, which is impermeable to oxygen, applied on the inside wall of the tyre covers. Unfortunately butyl rubber is not totally impermeable and the flow of oxygen into the body of the cover, though reduced, produces undesirable oxidation phenomena in the long term.

Other materials even more impermeable than butyl rubber have been proposed for the same purpose, as described for example in the documents US-A-5 236 030, US-A-4 874 670, US-A-5 036 113, EP-A-337 279, US-A-5 040 583 and US-A-5 156 921. These materials, however, are expensive and their use in tyre covers is associated with a number of problems.

Another way to avoid oxidation problems is to trap the oxygen chemically by the accelerated thermal oxidation of a rubber mix that acts as a buffer, located between a main source of oxygen and the zone to be protected against oxidation phenomena. For example, such a buffer composition may be located between the inside face of the tyre

cover, if necessary coated with butyl rubber, and the carcass ply to reduce the amount of oxygen that comes into contact with the said ply from the inflation air, especially in tyre covers intended for fitting to heavy goods vehicles.

To accelerate the fixing of oxygen it is known to use in these buffer compositions a metallic salt that catalyses the oxidation, in particular a cobalt salt. The effect of the salt is to activate the homolytic decomposition of the hydroperoxides generated during the ageing brought about by the aforesaid oxidation phenomena. The salt is introduced into the buffer composition preferably in amounts of 0.2 to 0.3 parts by weight of cobalt equivalent per 100 parts by weight of the elastomer. This increases the amount of oxygen that can be trapped by the buffer composition by around 50 to 100% compared with the same composition containing no cobalt salt.

Unfortunately, experience shows that this improvement of the oxidation-related behaviour is accompanied by a substantial increase of the hysteresis losses of the buffer composition owing to the considerable quantity of cobalt salt introduced. This increase of the hysteresis losses leads on the one hand to self-heating of the composition and hence to shorter life, contrary to the purpose intended, and on the other hand to an increase of the rolling resistance, which should also be avoided since manufacturers strive to limit the rolling resistance as much as possible in order to reduce fuel consumption.

For these reasons the use of buffer compositions, attractive as it may sound, has not developed as expected.

European patent document EP-A-507 207 describes a method for trapping oxygen by means of an elastomeric buffer composition contained in a wrapping layer. The buffer composition is characterised in particular by the presence of a transitional metal salt provided to activate the fixing of oxygen. As explained above, the metal salts described as preferred are cobalt salts. As subsidiaries, other metals such as manganese or even iron are also envisaged, but not in relation to specified salts.

Unexpectedly, the applicant has found that the aforementioned drawbacks can be greatly reduced by using specific iron salts in place of cobalt salts in these buffer compositions. Thus in accordance with the present invention, there is provided a product based on rubber, of the type including at least one buffer zone provided in order to trap oxygen external to said product so as to protect from oxidation at least one sensitive zone of said product, in which the or each said buffer zone contains a basic composition of at least one elastomer containing at least one salt of iron (III) provided to activate oxidation in said composition,

characterised in that said salt is the iron (III) salt of a carboxylic acid having the general formula $C_nH_{2n}O_2$ in which n is from 2 to 5.

It is particularly advantageous for the said salt to be iron (III) pentanoate or iron (III) acetate.

Preferably, the quantity of the said iron (III) salt according to the invention present in the composition may range from 0.01 to 0.03 pbw of equivalent iron, where the abbreviation "pbw" means "parts by weight per 100 parts by weight of the elastomer or totality of elastomers present in the composition". More preferably still, the quantity of iron (III) salt according to the invention ranges from 0.01 to 0.02 pbw of equivalent iron.

The composition according to the invention is based on natural or synthetic rubber, or a blend of two or more such rubbers. Examples of the synthetic rubbers suitable for use in the composition according to the invention are diene rubbers such as polyisoprene, polybutadiene, mono-olefin rubbers such as polychloroprene, polyisobutylene, the copolymers styrene-butadiene or styrene-butadiene-isoprene, the copolymers acrylonitrile-butadiene-styrene and the terpolymers ethylene-propylene-diene. Among the synthetic rubbers the diene rubbers are preferred, in particular any homopolymer obtained by polymerisation of a conjugated diene monomer having 4 to 12 carbon atoms,

or any copolymer obtained by co-polymerisation of one or more dienes conjugated either between themselves or with one or more vinyl aromatic compounds having from 8 to 20 carbon atoms.

Suitable conjugated dienes are, in particular, 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-di(C1 to C5 alkyl)-1,3-butadienes such as, for example, 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, phenyl-1,3-butadiene, 1,3-pentadiene and 2,4-hexadiene.

Suitable vinyl aromatic compounds are, for example, styrene, ortho-, meta- and para-methylstyrene, the commercial mixture "vinyl-toluene", para-tertiobutylstyrene, the methoxy-styrenes, the chloro-styrenes, vinylmesitylene, divinyl benzene, vinyl naphthalene, etc.

The co-polymers may contain for example between 99% and 20% by weight of diene units and between 1% and 80% by weight of vinyl aromatic units.

The polymers may have any microstructure, which is a function of the polymerisation conditions used, in particular the presence or absence of a modifying and/or randomising agent and the quantities of modifying and/or randomising agent used. The polymers may for example be block, statistical, sequenced or micro-sequenced polymers, etc., and may be prepared in a dispersion or in solution.

Preferred diene synthetic rubbers are the polybutadienes and in particular those having a content of 1,2-units between 4% and 80% and those having a content of cis-1,4 bonds of more than 90%, the polyisoprenes, butadiene-styrene co-polymers and in particular those having a styrene content 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 between 4% and 65%, and a content of trans-1,4 bonds between 30% and 80%, these having a total aromatic compound content between 5% and 50%, and a glass transition temperature

(Tg) between 0°C and 80°C, in particular those having a styrene content of between 25% and 30% by weight, a content of vinyl bonds of the butadiene part between 55% and 65%, a content of trans-1,4 bonds between 20% and 25% and a glass transition temperature between -20°C and -30°C.

In the case of butadiene-styrene-isoprene co-polymers, the suitable ones are those having a styrene content between 5% and 50% by weight and more particularly between 10% and 40%, an isoprene content between 15% and 60% by weight and more particularly between 20% and 50% by weight, a butadiene content between 5% and 50% and more particularly between 20% and 40% by weight, a content of 1,2-units of the butadiene part between 4% and 85%, a content of trans-1,4 units of the butadiene part between 6% and 80%, a content of 1,2- plus 3,4-units of the isoprene part between 5% and 70%, and a content of trans-1,4 units of the isoprene part between 10% and 50%.

The synthetic rubbers may be coupled and/or starred or alternatively functionalised with a coupling and/or starring or functionalising agent.

These rubbers may be vulcanised and or cross-linked by any of the known agents, such as sulphur, the peroxides, the bismaleimides, etc.

The composition according to the invention contains the usual fillers and additives such as carbon black, silica or any other reinforcing filler, stearic acid, reinforcing resins, zinc oxide, activators, pigments, vulcanisation accelerators or retarders, anti-ageing agents such as anti-oxidants, anti-reversion agents, oils or various agents to facilitate use, tackiness promoting resins, metal adhesion promoters, anti-ozone waxes, silicon binding and/or covering agents, etc.

The compositions according to the invention can be used in a wide variety of applications and notably for numerous rubber products, for example in tyre covers as buffer compositions between a source of oxygen, in particular inflation air or the external

atmosphere and a zone to be protected in the tyre cover. For example, these compositions may be used inside the internal calendering rubber, between this and the carcass ply, between the carcass ply and the crown plies, between the crown plies and the tread, between the carcass ply and the side walls, or even on the outside of the side walls.

A tyre cover according to the invention, the said cover being of the type comprising internal calendering rubber, a carcass ply extending from one bead wire to the other, crown plies, side walls ending in beads comprising at least one bead wire, and a tread, is characterised in that the said or each such buffer zone containing the said composition occupies at least one of the following positions:

radially inside the said calendering rubber, between the said internal calendering and the said carcass ply, between the said carcass ply and the said crown plies, between the said crown plies and the said tread, between the said carcass ply and the said side walls, inside or outside the said side walls, and inside or outside the said tread.

The use of the iron compound according to the invention is very different from the known uses of iron compounds in the rubber industry, for example their known use as oxidising salts to promote the mastication of rubbers (peptising properties) or devulcanisation for recycling, these applications being described, for example, in the documents US-A-3 324 100, EP-A-157 079 and RU-A-2 014 339.

As regards the process for obtaining a rubber-based product according to the present invention, this consists in incorporating the said iron (III) salt in the elastomer or elastomers contained in the buffer composition by working it in mechanically, to obtain the corresponding buffer zone.

According to another characteristic of the process, it consists in incorporating the said iron (III) salt in the said elastomer(s) at the same time as a filler intended to reinforce the said composition.

As regards the process according to the present invention for reducing the rolling resistance of a tyre cover, this consists in incorporating an iron (III) salt as defined above in an elastomer or in the elastomers constituting the said tyre cover, by working it in mechanically.

The invention will be easily understood with the help of the non-limiting examples given below.

These examples are either examples according to the invention, or ones not according to the invention that use compositions without any metallic derivative, or ones containing cobalt salts or even iron (III) salts that do not have the formula according to the invention specified earlier.

The oxidation-promoting efficacy of the iron or cobalt compounds is assessed by subjecting the compositions to ageing by thermal oxidation. The oxygen uptake is then measured by element analysis and the changes in mechanical properties such as the modulus, hysteresis loss and rupture properties are determined.

The tests are carried out under the following conditions:

Vulcanisation

Unless otherwise indicated, all the tests were carried out on specimens vulcanised by curing for 20 to 30 min at 150°C.

Ageing by thermal oxidation

A ventilated stove at 85°C is used. This temperature is regarded as representative of the temperatures encountered during the operation of tyre covers.

Hysteresis loss

The hysteresis loss, or hysteresis (Ph) is measured by determining the energy lost on rebound compared with the energy put in at 60°C, considering the sixth shock. The value, expressed as a percentage, is the difference between the energy supplied and the energy returned, referred to the energy supplied. The deformation for the losses measured is 40%.

Tensile tests

The strain modulus at 10% strain (M10) and at 100% strain (M100) are determined, in accordance with the standard ISO 37.

Scott fracture indexes

The rupture stress (Cr) in MPa and the elongation at rupture (Ar) in % are also determined. All these tensile measurements are effected under normal temperature and humidity conditions according to ISO 37.

EXAMPLES

In the two examples below, the following basic composition is used, this being prepared in a way known as such by using an internal mixer and then an external mixer. All the figures indicated are parts by weight, and it is to be made clear that the iron (III) is introduced into the internal mixer, for example a Banburry, at the same time as the carbon black, the ZnO, the stearic acid and the 6PPD.

Natural rubber	100
Carbon black N326	47
Sulphur	4.5
DCBS	0.8
ZnO	7.5
Stearic acid	0.9
6PPD	1.5

in which:

DCBS: N,N-dicyclohexyl-2-benzothiazolesulphenamide

6PPD: N-1,3-dimethylbutyl-N'-phenyl-paraphenylene diamine.

Starting with this basic composition, the following compositions are prepared for each of the two following example embodiments.

Example 1

Control compositions:

- Composition T1: basic composition with no metallic derivative.
- Composition T2: basic composition containing in addition 0.25 pbw of cobalt equivalent in the form of cobalt naphthenate.
- Composition T3: basic composition containing in addition 0.02 pbw of iron equivalent in the form of ferric acetylacetonate.

Preferred composition according to the invention

- Composition I1: basic composition containing in addition 0.02 pbw of iron equivalent in the form of iron (III) acetate.

As regards the aforementioned vulcanisation at 150°C, it should be noted that this lasted 20 min for each control composition T2, but 30 min for the other compositions.

2-a) Using these compositions, the strain module M10 and M100 and the hysteresis losses (hysteresis) were determined. The results are shown in Table 1 below.

Table 1

	T1	T2	T3	**I1**
M10 (MPa)	4.5	5.8	4.5	**4.5**
M100 (MPa)	2.2	2.6	2.3	**2.3**
Ph (%)	17	19	16.5	**16.5**

Table 1 shows that the iron (III) salt of acetic acid, in composition I1 according to the invention, modifies the characteristics of the basic composition less than does cobalt naphthenate in control composition T2, and that the relative hysteresis loss of composition I1 is considerably lower than that of the said control composition T2.

2-b) Experiments were carried out to demonstrate the ability of composition I1 to fix oxygen after thermal oxidation for 2 weeks at 85°C, comparing it with the control compositions T1, T2 and T3.

The results of these thermal oxidation tests are shown in Table 2 below, which gives the percentage by weight of oxygen fixed.

Table 2

	T1	T2	T3	**I1**
At 85°C 2 weeks	0.8	1.1	1.4	**1.3**

Table 2 shows that the iron (III) salt of acetic acid enables composition I1 to fix a larger amount of oxygen than control composition T2 containing cobalt naphthenate, the amount fixed being substantially larger compared with that of control composition T1 containing no iron or cobalt compound.

Basic compositions containing other metallic salts described as oxidation promoters in the literature, introduced in amounts such as to give an isomolar quantity of metal in relation to control composition T2, such as the salts of manganese (II) or (III) and in particular the carbonate, acetate or acetylacetonate of manganese (II), manganese (III) acetylacetonate, the salts of molybdenum (IV) and in particular molybdenum (IV) sulphide and oxide, the salts of copper (II) and in particular copper (II) hydroxide, carbonate, stearate, acetate or acetylacetonate, the salts of chromium (III) and in particular chromium acetylacetonate, and cerium (IV) sulphate, lead to results similar to those obtained with control composition T1 which contains no metallic salt.

2-c) Experiments were also carried out to determine the moduli and rupture properties and the hysteresis of composition I1 according to the invention compared with the control compositions T1, T2 and T3, after applying to each composition the aforesaid treatment of ageing by thermal oxidation (at 85°C for 2 weeks).

The results are given in Table 3 below, which shows, for each composition, the change in the values of the various parameters compared with those for the same composition before the thermal oxidation treatment.

Table 3

	T1	T2	T3	**I1**
M10	+60%	+ 55%	61%	**+56%**
M100	122%	+111%	-	-
Ph	+5.5	+ 11	+ 8	**+8**
Ar	-71%	-78%	-85%	**-80%**
Cr	-63%	-71%	-77%	**-73%**

In relation to the results of paragraph 2-b), this Table 3 shows that composition I1 according to the invention shows an ability to fix oxygen which is distinctly better compared with the said known composition T2, whereas following the treatment by thermal oxidation, it shows mechanical elongation and rupture properties which have evolved almost analogously after the thermal oxidation treatment.

Example 2:

Control compositions:

- Composition T1: basic composition with no metallic derivative.
- Composition T2: basic composition containing in addition 0.25 pbw of cobalt equivalent in the form of cobalt naphthenate.
- Composition T3: basic composition containing in addition 0.25 pbw of iron equivalent in the form of iron (III) fumarate.
- Composition T4: basic composition containing in addition 0.25 pbw of iron equivalent in the form of iron (III) gluconate.

- Composition T5: basic composition containing in addition 0.25 pbw of iron equivalent in the form of iron (III) citrate.

Preferred composition according to the invention:

- Composition I2: basic composition containing in addition 0.02 pbw of iron equivalent in the form of iron (III) pentanoate.

As regards the aforesaid vulcanisation at 150°C, it should be noted that this was carried out for 20 min in the case of control composition T2, whereas for the other compositions the time was 30 min.

2-a) With these compositions the strain moduli M10 and M100 and the hysteresis losses (or hysteresis) were determined. The results are given in Table 4 below.

Table 4:

	T1	T2	**I2**
M10 (MPa)	4.5	5.5	**4.2**
M100 (MPa)	2.2	2.4	**2.2**
Ph (%)	15.7	19.2	**15.6**

Table 4 shows that iron (III) salt of pentanoic acid in composition I2 according to the invention modifies the characteristics of the basic composition to a lesser extent than does the cobalt compound in control composition T2, and that the hysteresis loss of the said composition I2 is considerably smaller than that of the said control composition T2.

2-b) Experiments were carried out to demonstrate the ability of composition I2 to fix oxygen, after thermal oxidation for 2 weeks at 85°C, compared with the control compositions T1 and T2.

The results of these thermal oxidation tests are shown in Table 5 below, which gives the percentage by weight of oxygen fixed.

Table 5:

	T1	T2	**I2**
At 85°C 2 weeks	0.9	1.1	**1.4**

Table 5 shows that the iron (III) salt according to the invention results in oxygen fixing by composition I2 which is greater than that obtained with control composition T2 containing cobalt, and that the fixing is considerably greater than that achieved by control composition T1 which contains no iron or cobalt compound.

Basic compositions containing other metallic salts described as oxidation promoters in the literature, introduced in amounts such as to give an isomolar quantity of metal in relation to control composition T2, such as the salts of manganese (II) or (III) and in particular the carbonate, acetate or acetylacetonate of manganese (II), manganese (III) acetylacetonate, the salts of molybdenum (IV) and in particular molybdenum (IV) sulphide and oxide, the salts of copper (II) and in particular copper (II) hydroxide, carbonate, stearate, acetate or acetylacetonate, the salts of chromium (III) and in particular chromium acetylacetonate, and cerium (IV) sulphate, lead to results similar to those obtained with control composition T1 which contains no metallic salt.

2- c) Experiments were also carried out to determine the moduli and rupture properties and the hysteresis of composition I2 according to the invention compared with the control compositions T1 and T2, after applying to each composition the aforesaid treatment of ageing by thermal oxidation (at 85°C for 2 weeks).

The results are given in Table 6 below, which shows, for each composition, the change in the values of the various parameters compared with those for the same composition before the thermal oxidation treatment.

Table 6:

	T1	T2	**I2**
M10	+46%	+60%	**+75%**
M100	113%	129%	-
Ph	+ 7%	+ 8%	-
Ar	-74%	-79%	**-87%**
Cr	-64%	-68%	**-80%**

In relation to the results of paragraph 2-b), this Table 6 shows that composition I2 according to the invention shows an ability to fix oxygen which is distinctly better compared with the known compositions T1 and T2, whereas following the treatment by thermal oxidation, it shows mechanical elongation and rupture properties which have evolved almost analogously after the thermal oxidation treatment.

2-d) The quantity of oxygen fixed in the compositions not according to the invention containing iron compounds (compositions T3 to T5) was determined.

Oxygen fixing tests following the said thermal oxidation treatment mentioned in paragraph 2-b) were carried out.

The results are given in Table 7 below, whose presentation is analogous to that of Table 5 (percent by weight of oxygen fixed).

Table 7:

	T1	T2	T3	T4	T5
At 85°C 2 weeks	0.9	1.1	0.9	0.9	0.9

It is therefore apparent that the control compositions T3 to T5, which contain iron compounds not according to the invention, have less ability to fix oxygen than control composition T2 containing a cobalt derivative, and approximately the same ability as composition T1 which contains no metallic salt.

From the above examples it emerges that a rubber composition according to the invention, i.e. one which, like the said composition I2, contains an iron (III) salt of a carboxylic acid having the general formula $C_nH_{2n}O_2$ in which n is from 2 to 5, makes possible a considerable reduction of the metal content in the said composition compared with the known compositions, while at the same time appreciably improving the oxygen fixing characteristics.

It also emerges from these examples that a rubber composition according to the invention is characterised by hysteresis losses which are much lower compared with those of the known compositions.

It follows that the use of a rubber composition according to the invention in a tyre cover makes it possible, in particular, on the one hand to reduce significantly the rolling resistance of the said tyre and on the other hand to improve its endurance.

Needless to say, the invention is not limited to the examples described above.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Product based on rubber, of the type including at least one buffer zone provided in order to trap oxygen external to said product so as to protect from oxidation at least one sensitive zone of said product, in which the or each said buffer zone contains a basic composition of at least one elastomer containing at least one salt of iron (III) provided to activate oxidation in said composition,

characterised in that said salt is the iron (III) salt of a carboxylic acid having the general formula $C_nH_{2n}O_2$ in which n is from 2 to 5.

2. Product based on rubber according to Claim 1, characterised in that said iron (III) salt is iron (III) acetate.

3. Product based on rubber according to Claim 1, characterised in that the said iron (III) salt is iron (III) pentanoate.

4. Product based on rubber according to any one of the preceding claims, characterised in that the quantity of said iron (III) salt in said composition ranges from 0.01 to 0.03 percent by weight of iron equivalent.

5. Tyre cover, characterised in that it consists of a product based on rubber according to any one of the preceding claims.

6. Tyre cover according to Claim 5, said tyre cover being of the type which includes an internal calendering rubber, a carcass ply that extends from one bead wire to the other, crown plies, side walls that end in beads including at least one bead wire, and a tread, characterised in that the or each said buffer zone containing said composition occupies at least one of the following positions:

radially inside said internal calendering rubber, between said calendering rubber and said carcass ply, between said carcass ply and the crown plies, between said crown plies and the tread, between said carcass pply and the side walls, inside or outside said side walls, and/or inside or outside said tread.

7. Process for obtaining a product based on rubber according to any one of Claims 1 to 4, characterised in that the process consists of incorporating by mechanical work said salt of iron (III) into the elastomer or elastomers contained in the said composition, to obtain the or each said buffer zone.

8. Process for obtaining a product based on rubber according to Claim 7, said product including a reinforcing filler, characterised in that the process consists of incorporating said iron (III) salt into said elastomer or elastomers at the same time as the reinforcing filler provided to reinforce said composition.

9. Process for reducing the rolling resistance of a tyre cover, characterised in that the process consists of incorporating by mechanical work, into an elastomer or elastomers constituting the said tyre cover, a salt of iron (III) as defined in any one of Claims 1 to 4.

DATED this 19th day of June 2003

SOCIETE DE TECHNOLOGIE MICHELIN AND MICHELIN RECHERCHE ET TECHNIQUE S.A.

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

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