Title: SELF-SEALING TYRE AND METHOD OF MANUFACTURE

Abstract: Self-sealing tyre comprising at least one layer of sealing material having the following characteristics: (a) a value of the dynamic elastic modulus (G'), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is at least 60% lower than the value of said modulus measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 1%; (b) a value of the dynamic elastic modulus (G'), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is not less than 0.05 kPa, preferably in the range from 0.1 kPa to 0.4 kPa.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes andAbbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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5 The present invention relates to a self-sealing tyre for vehicle wheels.

More particularly, the present invention relates to a self-sealing tubeless tyre for vehicle wheels, to a process for manufacturing said tyre, and to a sealing material used therein.

In the industrial field of tyres for vehicle wheels, various attempts have been made to produce self-sealing tyres, in other words tyres which can retard or prevent the loss of air and their consequent deflation following a puncture caused by a sharp object (a nail, for example).

In the known art, descriptions have been given of self-sealing tyres provided with at least one layer comprising a polymeric material which can adhere to the object causing the puncture and can also flow into the puncture site when said object is removed, thus sealing the puncture and preventing the outflow of air from the tyre.

For example, US Patent 3,981,342 describes a self-sealing tubeless tyre provided with a layer including a composition comprising a mixture of a low molecular weight liquid elastomer and a high molecular weight solid elastomer, and a quantity of a cross-linking agent sufficient to give a partial cross-linking of said mixture, said liquid elastomer being present in a greater quantity than said solid elastomer. Examples of low molecular weight liquid elastomers which can be used according to the invention are: liquid cis-polyisoprene (for example, heat-depolymerized natural rubber, or low molecular weight depolymerized cis-polyisoprene); liquid polybutadiene; liquid polybutene; liquid EPDM; liquid butyl rubber. Examples of high molecular weight elastomers which can be used according
to the invention are highly unsaturated rubbers such as, for example, isoprene homopolymers (particularly natural or synthetic cis-polyisoprene); polybutadiene (particularly with a high cis content); polychloroprene; copolymers containing a major proportion of conjugated dienes (butadiene, for example) and a minor proportion of copolymerizable monomers containing monoethylenically unsaturated monomers (styrene or acrylonitrile, for example).

Alternatively, it is possible to use elastomers with a low degree of unsaturation such as butyl rubbers (isooolefin copolymers, for example isobutylene, with small quantities of dienes, for example isoprene), or EPDM-type rubbers (copolymers of at least two different monoolefins such as ethylene and propylene with a small quantity of a non-conjugated diene such as dicyclopentadiene, 1,4-hexadiene, 5-ethylidene-2-norbornene). Finally, it is also possible to use saturated elastomers such as EPM or ethylene-vinyl acetate copolymers. Examples of cross-linking agents which can be used according to the invention are: sulphur or sulphur donors; quinones; organic peroxides; polyisocyanates; and tetrahydrocarbyl titanate esters. Said layer would be able to impart self-sealing properties to the tyre.

US Patent 4,140,167 describes a sealing material usable, in particular, in the field of tyres. In the tyre, said sealing material can consist of a single layer, or a composite laminar structure. Preferably, said composite laminar structure comprises at least five layers of elastomeric material of which: two outer layers comprising an elastomeric material and an agent for retarding cross-linking by radiation, two inner layers comprising an elastomeric material and an agent for promoting cross-linking by radiation, and one layer, located between said two inner layers, comprising said sealing material which is at least partially degradable by radiation, or by heat in the
presence of a peroxide. Examples of materials which are
degraded by radiation, or by heat in the presence of a
peroxide, useful according to the invention are
polyisobutylene and its copolymers, or polyethylene
oxide. Said sealing material would be able to impart
self-sealing properties to the tyre.

US Patent 4,228,839 describes a self-sealing tyre
provided with a layer comprising a mixture of a
radiation-degradable polymeric material and a polymeric
material which can be cross-linked by radiation and/or
by heat. The degradable polymeric material can be
selected from: polyisobutylene; copolymers of
isobutylene with: conjugated olefins such as 1,3-
butadiene, isoprene, 2,3-methylbutadiene, or with vinyl
aromatic monomers such as styrene and alpha-methyl
styrene, or with vinyl polar monomers such as
acrylonitrile, methylvinyl acrylate, methylvinyl
lactone. The cross-linkable polymeric material can be
selected from natural rubber; styrene/butadiene
copolymers; polybutadiene; polyisoprene; block
copolymers, for example styrene/butadiene/styrene;
halogenated butyl rubbers, for example chlorobutyl
rubber; ethylene-propylene terpolymers; butadiene-
arconitrile copolymers; neoprene. Said layer would be
able to impart self-sealing properties to the tyre.

Patent application EP 127 998 describes a tubeless
tyre in which the inner liner is a laminar structure
formed by two outer layers comprising a halogenated
butyl rubber and an inner layer comprising a butyl
rubber and a peroxide. After vulcanization, the butyl
rubber of said inner layer would be degraded, because
of the presence of the peroxide, thus producing a
polymeric material having a Mooney viscosity (ML 1+4)
in the range from 2 to 12. Said polymeric material
would be able to impart self-sealing properties to the
tyre.

US Patent 4,895,610 describes a self-sealing tyre
provided with a layer comprising a butyl rubber and a
peroxide. Preferably, said layer comprises: 100 parts of butyl rubber; about 10 to 40 parts of carbon black; about 5 to 35 parts of polyisobutylene; about 5 to 35 parts of an oil; about 0 to 1 parts of sulphur; and about 1 to 8 parts of a peroxide. During the vulcanization of the tyre, the butyl rubber, in the presence of the peroxide, would be capable of being partially cross-linked, thus providing dimensional stability to said layer, and also of being partially degraded, thus providing a low-viscosity tacky material capable of imparting self-sealing properties to said tyre.

In the Applicant’s opinion, one of the major problems encountered in self-sealing tyres is that of finding a correct combination of properties for the sealing material used. Infact, said material must be able to flow rapidly towards the puncture, to adhere to the object causing the puncture, and to not flow out of the puncture, in order to prevent the loss of air and the consequent deflation of the tyre. Furthermore, the sealing material must maintain its position inside the tyre when the vehicle is halted or during storage. On the other hand, when the tyre is made to move, which could potentially create non-uniformities in the distribution of the sealing material, said sealing material must be capable of being rearranged rapidly and uniformly inside the tyre. Infact, a displacement of the sealing material from its original position and its accumulation in other areas of the tyre would not only cause a loss of balance in the weight distribution within the tyre, but would also make its use as a sealing layer ineffective, or would at least impart an unsatisfactory self-sealing capacity to the tyre. The sealing material must also be capable of being applied during the building of the tyre, thus avoiding the need to subject the finished tyre to further post-production treatments.
The Applicant has now found that it is possible to obtain the desired combination of properties by using a sealing material whose dynamic elastic modulus ($G'$) measured at high deformations (5%) is significantly lower than the value of said modulus measured at low deformations (1%).

In a first aspect, therefore, the present invention relates to a tyre for vehicle wheels, comprising:

- a carcass structure having at least one carcass ply shaped in a substantially toroidal configuration, whose opposite lateral edges are associated with respective right- and left-hand bead wires, each bead wire being incorporated in a respective bead;

- a belt structure comprising at least one belt strip applied in a circumferentially outer position with respect to said carcass structure;

- a tread circumferentially superimposed on said belt structure;

- a pair of sidewalls applied laterally on opposite sides with respect to said carcass structure;

- at least one layer of sealing material placed in a radially inner position with respect to said carcass ply;

in which said sealing material has the following characteristics:

(a) a value of the dynamic elastic modulus ($G'$), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is at least 60% lower than the value of said modulus measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 1%;

(b) a value of the dynamic elastic modulus ($G'$), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is not less than 0.05 KPa, preferably in the range from 0.1 KPa to 0.4 KPa.
In a preferred embodiment, said layer of sealing material is placed between said carcass ply and a layer of elastomeric material placed in a radially inner position with respect to said carcass ply.

In a further preferred embodiment, a further layer of elastomeric material is placed between said layer of sealing material and said carcass ply.

In a further preferred embodiment, said layer of sealing material extends over a surface substantially corresponding to the surface of development of said tread.

In a further preferred embodiment, a strip of elastomeric material, preferably having a substantially triangular cross section, is placed along each outer edge of said layer of sealing material.

In a further preferred embodiment, said layer of sealing material has a thickness in the range from 1.5 mm to 4.5 mm, preferably in the range from 2 mm to 4 mm.

In a further preferred embodiment, said sealing material is obtained by thermal degradation of a composition comprising at least one thermally degradable polymer. More preferably, said composition comprises:

- 100 phr of at least one thermally degradable polymer;
- from 50 phr to 150 phr, preferably from 55 phr to 120 phr, of at least one reinforcing filler;
- from 30 phr to 100 phr, preferably from 35 phr to 70 phr, of at least one plasticizer; and
- a quantity of not less than 10 phr, preferably in the range from 10 phr to 15 phr, of at least one organic peroxide.

In the present description and in the claims, the expression "phr" is intended to indicate the parts by weight of a given component per 100 parts by weight of polymer.
In a further aspect, the present invention relates to a process for producing tyres for vehicle wheels, said process comprising the following steps:

- making at least one coating layer of cross-linkable elastomeric material on an outer surface of a toroidal support the shape of which substantially matches that of the inner surface of the tyre;

- making at least one layer consisting of a composition comprising at least one thermally degradable polymer in a circumferentially outer position with respect to said coating layer of cross-linkable elastomeric material;

- applying at least one carcass ply in a circumferentially outer position with respect to said layer consisting of a composition comprising at least one thermally degradable polymer;

- applying a belt structure in a circumferentially outer position with respect to said carcass structure;

- applying a tread in a circumferentially outer position with respect to said belt structure;

- applying at least one pair of sidewalls on said carcass structure in laterally opposing positions;

- subjecting the green tyre to moulding in a mould cavity formed in a vulcanization mould;

- subjecting said green tyre to cross-linking by heating to a predetermined temperature and for a predetermined period;

in which, at the end of said cross-linking, said composition comprising at least one thermally degradable polymer has the following characteristics:

(a) a value of the dynamic elastic modulus ($G'$), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is at least 60% lower than the value of said modulus measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 1%;
(b) a value of the dynamic elastic modulus \( (G') \), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is not less than 0.05 KPa, preferably in the range from 0.1 KPa to 0.4 KPa.

In a preferred embodiment, the step of cross-linking is carried out by heating the green tyre to a temperature in the range from 100°C to 250°C, preferably from 120°C to 200°C.

In a further preferred embodiment, said layer consisting of a composition comprising at least one thermally degradable polymer is obtained by winding at least one ribbon-like band consisting of said composition comprising at least one thermally degradable polymer in close coils along the cross-sectional profile of a toroidal support. Said ribbon-like band may be produced, for example, by extruding said composition comprising at least one thermally degradable polymer. Further details of the methods of forming and/or depositing the various components of the tyre on a toroidal support are described, for example, in patent applications EP 943,421, EP 919,406 and WO 01/36185 in the name of the present Applicant.

In a further aspect, the present invention relates to a sealing material having the following characteristics:

(a) a value of the dynamic elastic modulus \( (G') \), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is at least 60% lower than the value of said modulus measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 1%;

(b) a value of the dynamic elastic modulus \( (G') \), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is not less than 0.05 KPa, preferably in the range from 0.1 KPa to 0.4 KPa.
In a preferred embodiment, the thermally degradable polymer which can be used according to the present invention can be selected from homopolymers of at least one alpha-olefin having from 3 to 12 atoms of carbon or its derivatives; copolymers of at least one alpha-olefin having from 3 to 12 carbon atoms, with at least one olefin selected from: ethylene, conjugated or non-conjugated dienes having from 4 to 20 carbon atoms, or mixtures thereof.

Examples of alpha-olefins which can be used according to the present invention are: propylene, 1-butene, isobutene, 1-pentene, 1-hexene, 1-octene, or mixtures thereof.

Examples of diene monomers which can be used according to the present invention are: 1,3-butadiene, isoprene, 1,4-hexadiene, 1,4-cyclohexadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, vinylnorbornene, or mixtures thereof.

Thermally degradable polymers which are particularly preferred are: polypropylene; butyl rubber; ethylene/propylene copolymers containing not more than 5% by weight of ethylene, preferably not more than 1% by weight; ethylene/propylene/diene terpolymers containing not more than 5% by weight of ethylene, preferably not more than 1% by weight, and not more than 5% by weight of diene, preferably not more than 1% by weight.

Even more preferably, the thermally degradable polymer is selected from butyl rubbers. Butyl rubbers are produced by copolymerization of isobutene with a small quantity of isoprene. Butyl rubbers generally contain from about 1% by weight to about 5% by weight of isoprene-derived repeated units and from about 95% by weight to about 99% by weight of isobutene-derived repeated units. Butyl rubbers which can be used advantageously according to the present invention have an average molecular weight in the range from 200,000 to 500,000, preferably from 300,000 to 400,000.
Examples of butyl rubbers which can be used in the present invention and are currently available on the market are the Bayer Butyl® products made by Bayer.

In a preferred embodiment, the reinforcing filler can be selected from carbon black, silica, alumina, aluminosilicates, calcium carbonate, kaolin, or mixtures thereof. Carbon black is preferred.

The types of carbon black which can be used according to the present invention can be selected from those conventionally used in the production of tyres which generally have a surface area of not less than 20 m²/g (determined by absorption of CTAB as described in the ISO 6810 standard).

The silica which can be used according to the present invention can generally be a pyrogenic silica or, preferably, a precipitated silica, having a surface area BET (measured according to the ISO 5794/1 standard) in the range from 50 m²/g to 500 m²/g, preferably from 70 m²/g to 200 m²/g.

In a preferred embodiment, the plasticizer can be selected from: mineral oils, vegetable oils, synthetic oils, or mixtures thereof such as, for example, aromatic oil, naphthenic oil, phthalates, soya oil, or mixtures thereof. An aromatic oil is preferred.

In a preferred embodiment, the organic peroxide can be selected from organic peroxides having a high degradation temperature, preferably above 100°C. Specific examples of organic peroxides which can be used according to the invention are: 2,5-bis(t-butyl peroxy)-2,5-t-butylhexane, 1,1-di(t-butyl peroxy)-3,3,5-trimethyl cyclohexane, 2,5-dimethyl-2,5-di(t-butyl peroxy)hexene-3, p-chlorobenzyl peroxy, 2,4-dichlorobenzyl peroxy, 2,2-bis(t-butyl peroxy)butane, di-t-butyl peroxy, benzyl peroxy, 2,5-bis(t-butyl peroxy)-2,5-dimethylhexane, dicumyl peroxy, 2,5-dimethyl-2,5-di(t-butyl peroxy)hexane, or mixtures thereof. Dicumyl peroxy is preferred.
Said peroxides can be added to the polymeric material as such (100% active peroxide) or supported on inert fillers such as calcium carbonate, or can be dispersed in a silicone oil (from about 35% to about 60% of active peroxide).

Said thermally degradable composition can optionally comprise other additives commonly used in elastomeric compositions. For example, antioxidants, anti-ageing agents, adhesives, anti-ozone agents, modifying resins, or mixtures thereof can be added to said polymeric material.

The thermally degradable composition according to the present invention can be prepared by mixing the components indicated above with the other additives which may be present, according to methods known in the art. The mixing can be carried out, for example, by means of a mixer of the open-mill type, or an internal mixer of the type with tangential rotors (Banbury) or interlocking rotors (Intermix), or in continuous mixers of the Ko-Kneader (Buss) type or the twin-screw co-rotating or counter-rotating type.

The present invention will now be illustrated further by some examples of embodiment, with reference to the attached Fig. 1 and Fig. 2, which show a sectional view of a portion of the tyre made according to the invention.

The letter "a" indicates an axial direction, and "r" indicates a radial direction. For simplicity, Fig. 1 and Fig. 2 show only a portion of the tyre, the remaining portion, which is not shown, is identical and symmetrically arranged with respect to the radial direction "r".

The tyre (100) comprises at least one carcass ply (101) whose opposite lateral edges are associated with respective bead wires (102). The association between the carcass ply (101) and the bead wires (102), in this case, is achieved by folding back the opposite lateral edges of the carcass ply (101) around the bead wires
(102), so as to form the so-called carcass back-folds (101a) as shown in Fig. 1 and Fig. 2.

Alternatively, the conventional bead wires (102) can be replaced by a pair of circumferentially inextensible annular inserts formed by elongate elements arranged in concentric coils (not shown in Fig. 1 and Fig. 2) (see, for example, European patent applications EP 928,680 and EP 928,702). In this case, the carcass ply (101) is not back-folded around said annular inserts, the coupling being provided by a second carcass ply (not shown in Fig. 1 and Fig. 2) applied externally onto the first ply.

The carcass ply (101) generally consists of a plurality of reinforcing cords arranged parallel to each other and at least partially covered with a layer of elastomeric mixture. These reinforcing cords usually consist of textile fibres such as, for example, rayon, nylon, polyethylene terephthalate, or of steel wires which are stranded together, covered with a metal alloy (for example copper/zinc, zinc/manganese, zinc/molybdenum/cobalt alloys and the like).

The carcass ply (101) is usually of the radial type; in other words, it incorporates reinforcing cords arranged in a substantially perpendicular direction with respect to a circumferential direction. Each bead wire (102) is encased in a bead (103), defined along an inner circumferential edge of the tyre (100), with which the tyre engages on a rim (not shown in Fig. 1 and Fig. 2) forming part of a vehicle wheel. The space defined by each carcass back-fold (101a) contains a bead filler (104) in which the bead wires (102) are embedded. An anti-abrasion strip (105) is usually placed in an axially outer position with respect to the carcass back-fold (101a).

A belt structure (106) is applied along the circumferential development of the carcass ply (101). In the particular embodiment shown in Fig. 1 and Fig. 2, the belt structure (106) comprises two belt strips
(106a, 106b) which incorporate a plurality of reinforcing cords, typically metal cords, which are parallel to each other in each strip and intersecting with respect to the adjacent strip, orientated so as to form a predetermined angle with respect to a circumferential direction. At least one reinforcing layer (106c) can be optionally applied to the radially outermost belt strip (106b). In the particular embodiment shown in Fig. 1 and Fig. 2, two zero-degrees reinforcing layers (106c, 106d) are applied, these being commonly known as "0° belt", generally incorporating a plurality of reinforcing cords, typically textile cords, arranged at an angle of a few degrees with respect to a circumferential direction, and covered and welded together by means of an elastomeric material.

A sidewall (108), which extends, in an axially outer position, from the bead (103) to the end of the belt structure (106), is also applied externally to the carcass ply (101).

A tread (109), whose lateral edges are connected to the sidewalls (108), is applied circumferentially in a radially outer position with respect to the belt structure (106). Externally, the tread (109) has a rolling surface (109a) designed to come into contact with the ground. In this surface (109a), shown for simplicity as smooth in Fig. 1 and Fig. 2, there are generally made circumferential grooves which are connected by transverse notches (not shown in Fig. 1 and Fig. 2) so as to define a plurality of blocks of various shapes and sizes distributed over the rolling surface (109a).

In the connecting zone between the sidewalls (108) and the tread (109) there may optionally be present a strip of elastomeric material (110) commonly known as a "mini-sidewall", which is generally obtained by co-extrusion with the tread and enables the mechanical interaction between the tread (109) and the sidewalls
(108) to be improved. Alternatively, the end portion of the sidewall (108) is made to directly cover the lateral edge of the tread (109). Between the belt structure (106) and the tread (109) there may optionally be present a underlayer which forms, together with the tread (109), a structure commonly known as a "cap and base" (not shown in Fig. 1 and Fig. 2).

In the case of tubeless tyres, a layer of elastomeric material (111), generally called a "liner", can also be provided in a radially inner position with respect to the carcass ply (101), to provide the necessary impermeability to the inflation air of the tyre. A layer of sealing material (107) which can be made according to the present invention can be placed between the layer of elastomeric material (111) and the carcass ply (101). A further layer of elastomeric material (113), generally called a "under-liner", can also be provided above the layer of elastomeric material (111), as an additional means of ensuring the impermeability of the tyre to an inflating fluid when the tyre is fitted on a rim and inflated. Two strips of elastomeric material with an essentially triangular cross section (112) can optionally be placed along each outer edge of the layer of sealing material (107), as shown in Fig. 2. Said strips have the function of containing the sealing material in a specified area, thus preventing, for example, infiltrations of the material between the adjacent elements, particularly during the vulcanization of the tyre. Said infiltrations could cause problems of co-vulcanization and detachment of said elements, which would tend to detract from the performance and durability of the finished tyre.

The process for producing the tyre according to the present invention can be carried out according to technique and using apparatus that are known in the prior art, as described, for example, in the patents EP
199,064, US 4,872,822 and US 4,768,937, said process including at least one step of manufacturing the green tyre and at least one step of vulcanizing it.

More particularly, the process for producing the tyre comprises the steps of preparing beforehand and separately from each other a series of semi-finished articles corresponding to the different parts of the tyre (carcass plies, belt structure, bead wires, fillers, sidewalls and tread) which are subsequently associated with each other by means of suitable manufacturing machine generally comprising at least one building drum. Next, the subsequent step of vulcanization welds the aforesaid semi-finished articles together to produce a monolithic block, i.e. the finished tyre.

Naturally, the step of preparing the aforesaid semi-finished articles is preceded by a step of preparing and moulding the corresponding mixtures which are the constituents of said semi-finished articles, according to conventional techniques.

The green tyre produced in this way is then sent for the subsequent steps of moulding and vulcanization. To this end, a vulcanization mould is used which is designed to receive the tyre being processed inside a moulding cavity having walls which are countermoulded and which define the outer surface of the tyre when the vulcanization is complete.

Alternative processes for the production of a tyre or of parts thereof without making use of semi-finished articles are described, for example, in the patent applications EP 928,680 and EP 928,702 cited above.

The moulding of the green tyre can be carried out by introducing a pressurized fluid into the space delimited by the inner surface of the tyre, so as to press the outer surface of the green tyre against the walls of the moulding cavity. In one of the most widespread moulding methods, a vulcanization chamber of elastomeric material filled with steam and/or another
pressurized fluid is inflated inside the tyre which is enclosed in the moulding cavity. In this way, the green tyre is pushed against the inner walls of the moulding cavity, thus obtaining the desired moulding.

Alternatively, the moulding can be carried out without an inflatable vulcanization chamber, by providing inside the tyre a metallic toroidal support shaped according to the configuration of the inner surface of the tyre to be produced, as described, for example, in the patent EP 242,840. The difference in the coefficient of thermal expansion between the metallic toroidal support and the green elastomeric material is exploited to provide an appropriate moulding pressure.

At this point, the step of vulcanizing the green elastomeric material present in the tyre is carried out. For this purpose, the outer wall of the Vulcanization mould is brought into contact with a heating fluid (generally steam) in such a way that the outer wall reaches a maximum temperature generally in the range from 100°C to 230°C. At the same time, the inner surface of the tyre is brought to the Vulcanization temperature by using the pressurized fluid which is also used to press the tyre against the walls of the moulding cavity, heated to a maximum temperature in the range from 100°C to 250°C. The time required to obtain a satisfactory degree of vulcanization throughout the mass of the elastomeric material can generally vary from 3 to 90 minutes, and is mainly dependent on the dimensions of the tyre. When the vulcanization is complete, the tyre is removed from the vulcanization mould.

The present invention is further illustrated below by some examples of embodiment provided for guidance only and without restrictive intent.

**EXAMPLES 1 AND 2**

The compositions shown in Table 1 (the quantities of the various components have been expressed in phr) were prepared as follows.
All the components shown in Table 1 were loaded into a laboratory internal mixer of the type with tangential rotor (Banbury), model PL 1.6 made by Pomiini, which was rotated at approximately 40 r.p.m. After approximately three minutes, but in any case as soon as the temperature reached 120°C, said compositions were discharged from the mixer and then transferred to a laboratory open cylinder mixer.

TABLE 1

<table>
<thead>
<tr>
<th>EXAMPLE</th>
<th>1</th>
<th>2 (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIR</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Carbon black</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>Aromatic oil</td>
<td>40</td>
<td>35</td>
</tr>
<tr>
<td>Peroxide</td>
<td>10</td>
<td>8</td>
</tr>
</tbody>
</table>

(*) = control.

IIR: Isobutylene/isoprene copolymer having a degree of unsaturation of 1.75%±0.20 molar (Bayer Butyl® 301, a commercial product made by Bayer);

Polyisobutylene: Vistanex® LM-MS-LC, a commercial product made by Exxon Mobil;

Carbon black: N660 (Cabot);

Peroxide: Dicumyl peroxide (100% active peroxide; Perkadox BC-FF, a commercial product made by Akzo Nobel).

The compositions prepared in this way were subject to MDR rheometric analysis, using a Monsanto R.P.A. 2000 rheometer. For this purpose, cylindrical test specimens with weights in the range from 4.5 g to 5.5 g were obtained by punching from said non-degraded compositions, and were subjected to the following cycle:

1°: measurement of \( G' \) at 80°C, frequency 1 Hz, deformation 1% and 5%;

2°: heating of the test specimen to 200°C for 10 minutes;
3°: measurement of \((G')\) at 80°C, frequency 1 Hz, deformation 1% and 5%.

The results are shown in Table 2.

\begin{table}
\begin{tabular}{|l|c|c|}
\hline
EXAMPLE & 1 & 2 (*) \\
\hline
1°: \((G')\) at (1%) (KPa) & 99.50 & 89.13 \\
\hline
3°: \((G')\) at (1%) (KPa) & 0.765 & 0.383 \\
\hline
1°: \((G')\) at (5%) (KPa) & 56.384 & 56.920 \\
\hline
3°: \((G')\) at (5%) (KPa) & 0.153 & 0.230 \\
\hline
\end{tabular}
\end{table}

(*): control.

**EXAMPLE 3**

The compositions of Examples 1 and 2 were used to prepare the layer of sealing material for Pirelli P6000 @ 195/60R15 tyres. The tyres made in this way were punctured with a 4 mm nail at four points located at 90° to each other around the tyre. After extraction of the nail, no air flowed out of either tyre. The tyres were then left in storage for 15 days; at the end of this period, it was found that the tyre having the layer of sealing material produced from the composition of Example 1 (according to the invention) was still substantially inflated, while the tyre having the layer of sealing material produced from the composition of Example 2 (control) was deflated. An analysis of the two tyres revealed that the layer of sealing material produced from the composition of Example 2 (control) had not remained in position. In particular, it was found that said sealing material had accumulated on the
bottom of the tyre, thus causing the outflow of air from the upper holes.
1. Tyre for vehicle wheels, comprising:
- a carcass structure having at least one carcass ply shaped in a substantially toroidal configuration, whose opposite lateral edges are associated with respective right- and left-hand bead wires, each bead wire being enclosed in a respective bead;
- a belt structure comprising at least one belt strip applied in a circumferentially outer position with respect to said carcass structure;
- a tread circumferentially superimposed on said belt structure;
- a pair of sidewalls applied laterally on opposite sides with respect to said carcass structure;
- at least one layer of sealing material placed in a radially inner position with respect to said carcass ply;

in which said sealing material has the following characteristics:
(a) a value of the dynamic elastic modulus \( (G') \), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is at least 60% lower than the value of said modulus measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 1%;
(b) a value of the dynamic elastic modulus \( (G') \), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is not less than 0.05 KPa.

2. Tyre according to Claim 1, in which the sealing material has the following characteristics:
(a) a value of the dynamic elastic modulus \( (G') \), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is at least 60% lower than the value of said modulus
measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 1%;
(b) a value of the dynamic elastic modulus (G'), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is in the range from 0.1 KPa to 0.4 KPa.

3. Tyre according to Claim 1 or 2, in which said layer of sealing material is placed between said carcass ply and a layer of elastomeric material placed in a radially inner position with respect to said carcass ply.

4. Tyre according to Claim 3, in which a further layer of elastomeric material is placed between said layer of sealing material and said carcass ply.

5. Tyre according to any one of the preceding claims, in which said layer of sealing material extends over a surface substantially corresponding to the surface of development of said tread.

6. Tyre according to any one of the preceding claims, in which a strip of elastomeric material is placed along each outer edge of said layer of sealing material.

7. Tyre according to any one of the preceding claims, in which said layer of sealing material has a thickness in the range from 1.5 mm to 4.5 mm.

8. Tyre according to any one of the preceding claims, in which said sealing material is obtained by thermal degradation of a composition comprising at least one thermally degradable polymer.

9. Tyre according to Claim 8, in which said composition comprises:
   - 100 phr of at least one thermally degradable polymer;
   - from 50 phr to 150 phr of at least one reinforcing filler;
   - from 30 phr to 100 phr of at least one plasticizer; and
- 22 -

a quantity of not less than 10 phr of at least one organic peroxide.

10. Tyre according to Claim 8 or 9, in which the thermally degradable polymer is selected from homopolymers of at least one alpha-olefin having from 3 to 12 atoms of carbon or its derivatives; copolymers of at least one alpha-olefin, having from 3 to 12 carbon atoms, with at least one olefin selected from: ethylene, conjugated or non-conjugated dienes having from 4 to 20 carbon atoms, or mixtures thereof.

11. Tyre according to Claim 10, in which the thermally degradable polymer is selected from: polypropylene; butyl rubber; ethylene/propylene copolymers containing not more than 5% by weight of ethylene; ethylene/propylene/diene terpolymers containing not more than 5% by weight of ethylene and not more than 5% by weight of diene.

12. Tyre according to Claim 11, in which the thermally degradable polymer is selected from butyl rubbers.

13. Tyre according to any one of Claims 9 to 12, in which the reinforcing filler is selected from carbon black, silica, alumina, aluminosilicates, calcium carbonate, kaolin, and mixtures thereof.

14. Tyre according to Claim 13, in which the reinforcing filler is carbon black.

15. Tyre according to any one of Claims 9 to 14, in which the plasticizer is selected from: mineral oils, vegetable oils, synthetic oils, and mixtures thereof.

16. Tyre according to Claim 15, in which the plasticizer is an aromatic oil.

17. Tyre according to any one of Claims 9 to 16, in which the organic peroxide is selected from organic peroxides having a degradation temperature above 100°C.

18. Tyre according to Claim 17, in which the organic peroxide is dicumyl peroxide.

19. Process for producing tyres for vehicle wheels, said process comprising the following steps:
making at least one coating layer of cross-linkable elastomeric material on an outer surface of a toroidal support whose shape is essentially complementary to the inner surface of the tyre;

making at least one layer consisting of a composition comprising at least one thermally degradable polymer in a circumferentially outer position with respect to said coating layer of cross-linkable elastomeric material;

applying at least one carcass ply in a circumferentially outer position with respect to said layer consisting of a composition comprising at least one thermally degradable polymer;

applying a belt structure in a circumferentially outer position with respect to said carcass structure;

applying a tread in a circumferentially outer position with respect to said belt structure;

applying at least one pair of sidewalls on said carcass structure in laterally opposite positions;

subjecting the green tyre to moulding in a mould cavity formed in a vulcanization mould;

subjecting said green tyre to cross-linking by heating to a predetermined temperature and for a predetermined period;

in which, at the end of said cross-linking, said composition comprising at least one thermally degradable polymer has the following characteristics:

(a) a value of the dynamic elastic modulus \( G' \), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is at least 60% lower than the value of said modulus measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 1%;

(b) a value of the dynamic elastic modulus \( G' \), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is not less than 0.05 KPa.
20. Process according to Claim 19, in which, at the end of said cross-linking, said composition comprising at least one thermally degradable polymer has the following characteristics:

(a) a value of the dynamic elastic modulus \( (G') \), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is at least 60% lower than the value of said modulus measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 1%;

(b) a value of the dynamic elastic modulus \( (G') \), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is in the range from 0.1 KPa to 0.4 KPa.

21. Process according to Claim 19 or 20, in which the step of cross-linking is carried out by heating the green tyre to a temperature in the range from 100°C to 250°C.

22. Process according to any one of Claims 19 to 21, in which said layer consisting of a composition comprising at least one thermally degradable polymer is obtained by winding at least one ribbon-like band consisting of said composition comprising at least one thermally degradable polymer in close coils along the cross-sectional profile of a toroidal support.

23. Process according to any one of Claims 19 to 22, in which said composition comprises:

- 100 phr of at least one thermally degradable polymer;
- from 50 phr to 150 phr of at least one reinforcing filler;
- from 30 phr to 100 phr of at least one plasticizer; and
- a quantity of not less than 10 phr of at least one organic peroxide.

24. Process according to Claim 23, in which the thermally degradable polymer is defined according to any one of Claims 10 to 12.
25. Process according to Claim 23 or 24, in which the reinforcing filler is defined according to Claim 13 or 14.
26. Process according to any one of Claims 23 to 25, in which the plasticizer is defined according to Claim 15 or 16.
27. Process according to any one of Claims 23 to 26, in which the organic peroxide is defined according to Claim 17 or 18.
28. Sealing material having the following characteristics:
   (a) a value of the dynamic elastic modulus ($G'$), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is at least 60% lower than the value of said modulus measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 1%;
   (b) a value of the dynamic elastic modulus ($G'$), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is not less than 0.05 kPa.
29. Sealing material according to Claim 28, having the following characteristics:
   (a) a value of the dynamic elastic modulus ($G'$), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is at least 60% lower than the value of said modulus measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 1%;
   (b) a value of the dynamic elastic modulus ($G'$), measured at a temperature of 80°C, at a frequency of 1 Hz, with a deformation of 5%, which is in the range from 0.1 kPa to 0.4 kPa.
### A. CLASSIFICATION OF SUBJECT MATTER

**IPC 7** B29C73/22

According to International Patent Classification (IPC) or to both national classification and IPC

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

**IPC 7** B29C B60C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO–Internal

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td><strong>US 4 171 237 A (ANDERSON JOHN N ET AL)</strong>&lt;br&gt;16 October 1979 (1979-10-16)&lt;br&gt;column 3, line 62 —column 4, line 3;&lt;br&gt;figure 6; table 5&lt;br&gt;column 5, line 1 — line 19&lt;br&gt;column 5, line 44 — line 50</td>
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**X** Further documents are listed in the continuation of box C.  
**X** Patent family members are listed in annex.

**A** document defining the general state of the art which is not considered to be of particular relevance

**E** earlier document but published on or after the international filing date

**L** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

**O** document referring to an oral disclosure, use, exhibition or other means

**P** document published prior to the international filing date but later than the priority date claimed

**P** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

**X** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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**X** document member of the same patent family

Date of the actual completion of the international search: 17 December 2002

Date of mailing of the international search report: 30/12/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5816 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–8018

Authorized officer: Boone, J
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