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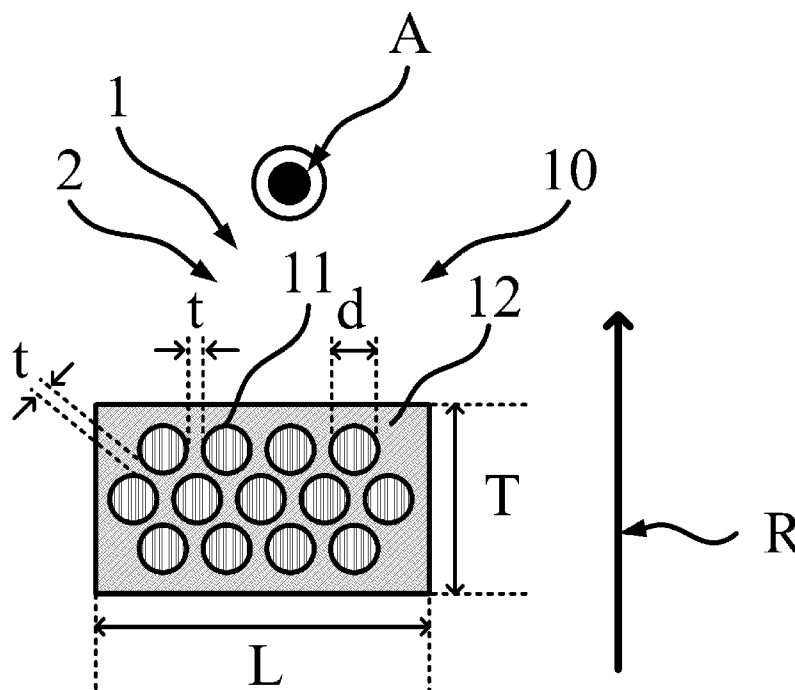
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(54) Title: AN ARTICLE, IN PARTICULAR A TIRE



(57) Abstract: The present invention relates to an article comprises a portion (10) comprising a rubber composition cured or intended to be cured at a curing temperature, the portion (10) provided with at least one external face (12) and at least one fiber (11) passing through the portion, the fiber (11) comprising a thermoplastic resin exhibiting a melting point higher than the curing temperature, the fiber (11) having a cross sectional area (s) on the external face (12). In one embodiment the the cross sectional area (s) of the fiber is being more than 1.0 mm². The invention is also related to production method of a cured article comprising at least a step of removing a fiber from said article.



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Description

Title of Invention: AN ARTICLE, IN PARTICULAR A TIRE

Technical Field

[0001] The field of the invention is that of articles, for example, tires, shoes, conveyors or caterpillar tracks, in particular for tire treads, and that of production methods of the articles.

Background Art

[0002] Articles, for example tires, comprise external portions, for example tire treads made of rubber compositions, and the external portions are provided with an incisions, slits, holes or combinations thereof in order to adjust the rigidities of the external portions and to improve performances of the articles as the following patent literature 1 discloses.

Citation List

Patent Literature

[0003] PTL 1: WO 2003/029031

PTL 2: EP 0925907

[0004] The articles having the external portions provide with the holes are industrially produced for example using methods described in the patent literature 2. In this type of method, the holes are formed using special tools such as needles or fingers which penetrate the portion on faces thereof during curing of the article. The form of the holes depends on that of the special tools, and there is some risk that the holes, the external portions other than the holes or both suffer damage from the special tools when the special tools remove from the external portions.

Summary of Invention

Technical Problem

[0005] During their research, the inventor has discovered that a specific portion of an article, for a rubber article, in particular a tire, a shoe, a conveyor or a caterpillar track tread, in more particular a tire and a specific production method of the article, which allows excellently producing an article comprising a portion provided with a hole(s) externally opening, without using the above special tools such as needles or fingers.

[0006] In the present description, unless expressly stated otherwise, all the percentages (%) indicated are percentages by weight (wt%).

[0007] The expression “elastomer matrix” is understood to mean, in a given composition, all of the elastomers present in said rubber composition.

[0008] The abbreviation “phr” signifies parts by weight per hundred parts by weight of the elastomer matrix in the considered rubber composition.

- [0009] In the present description, unless expressly indicated otherwise, each T_{gDSC} (glass transition temperature) is measured in a known way by DSC (Differential Scanning Calorimetry) according to Standard ASTM D3418-08.
- [0010] Any interval of values denoted by the expression “between a and b” represents the range of values of more than “a” and of less than “b” (i.e. the limits a and b excluded) whereas any interval of values denoted by the expression “from a to b” means the range of values going from “a” to “b” (i.e. including the strict limits a and b).
- [0011] The expression “based on” should be understood in the present application to mean a composition comprising the mixture(s), the product of the reaction of the various constituents used or both, some of the constituents being able or intended to react together, at least partly, during the various manufacturing phases of the composition, in particular during the vulcanization (curing).
- [0012] As a tire has a geometry of revolution about an axis of rotation, the geometry of the tire is generally described in a meridian plane containing the axis of rotation of the tire, and the following definitions of directions of the tire are understood in the present application:
- A radial direction is a direction perpendicular to the axis of rotation of the tire;
 - An axial direction is a direction parallel to the axis of rotation of the tire;
 - A circumferential direction is a direction perpendicular to the meridian plane.
- [0013] A plane being perpendicular to the axis of rotation of the tire and passing through the middle of a tread surface of the tire is referred to as an equatorial plane of the tire.
- [0014] In what follows, expressions “radially”, “axially” and “circumferentially” respectively mean “in the radial direction”, “in the axial direction” and “in the circumferential direction”. Expressions “radially on the inside (radially inner or radially internal), or respectively radially on the outside (radially outer or radially external)” mean “closer or, respectively, further away, from the axis of rotation of the tire, in the radial direction, than”. Expressions “axially on the inside (axially inner or axially interior) or respectively axially on the outside (axially outer or axially exterior)” mean “closer or, respectively further away, from the equatorial plane, in the axial direction, than”. Respective dimensions of a given element in the radial, axial and circumferential directions will also be denoted “radial thickness or height”, “axial width” and “circumferential length” of this element. Expression “laterally” means “in the circumferential or axial direction”.
- [0015] The expression “X extending substantially perpendicularly to Y” (or the expression “X substantially perpendicular to Y”) means the angle from the extending direction of X (or X) to Y is from 80 to 100 degrees, preferably from 85 to 95 degree.
- [0016] The expression “X extending substantially parallelly to Y” (or the expression “X substantially parallel to Y”) means the angle from the extending direction of X to Y is

from -10 to 10 degrees, preferably from -5 to 5 degree.

Solution to Problem

- [0017] A first aspect of the invention is an article comprising a portion (10) comprising a rubber composition cured or intended to be cured, preferably a cured rubber composition, at a curing temperature;
- the portion (10) provided with at least one external face (12) and at least one fiber (11) passing through the portion (10);
 - the fiber (11) comprising a thermoplastic resin exhibiting a melting point higher than the curing temperature; and
 - the fiber (11) having a cross section area (s) on the external face (12).
- [0018] According to a preferred embodiment of the first aspect, the curing temperature is between 110°C and 190°C. In particular, the curing time is between 5 and 90 min.
- [0019] The expression “external” face (12) means a face which is in contact either with the air or with an inflating gas.
- [0020] The thermoplastic (or thermosoftening plastic) is a plastic material, a polymer or a copolymer, that becomes pliable or moldable above a specific temperature and solidifies upon cooling.
- [0021] The melting point is a well-known basic physical constant (available, for example, in “Handbook of Chemistry and Physics”) of organic or inorganic compounds; it can be monitored by any known method, for example by the Thiele method, the Kofler bench method or else by DSC analysis.
- [0022] The fiber (11) has the cross sectional area on the external face (12) of the portion (10) of the article according to the first aspect, that is, the tip part of the fiber on the external face (12) is in contact either with the air or with an inflating gas.
- [0023] According to a preferred embodiment of the first aspect, the fiber (11) predominately comprises the thermoplastic resin, that is, the fiber (11) comprises more than 50% by weight of the thermoplastic resin per 100% by weight of the fiber (11), preferably the fiber (11) comprises more than 60%, more preferably more than 70%, still more preferably more than 80%, particularly more than 90%, by weight of the thermoplastic resin per 100% of the fiber (11).
- [0024] According to a preferred embodiment of the first aspect, the cross section of the fiber (11) on the external face (12) is polygonal, elliptical or circular.

Advantageous Effects of Invention

- [0025] The specific portion (10) (in particular, a tire tread, a shoe sole, a conveyor belt or a caterpillar track tread, in more particular a tire tread) of the article according to the invention and the specific production method according to the invention allow excellently producing an article comprising a portion (10) provided with a hole(s) (13)

externally opening, without using the above special tools such as needles or fingers.

[0026] A second aspect of the invention is the article according to the first aspect, wherein the cross sectional area (s) of the fiber (11) on the external face (12) is more than 1.0 mm² (for example, between 1.0 and 100.0 mm²), preferably more than 1.5 mm² (for example, between 1.5 and 60.0 mm²), more preferably more than 1.5 mm² (between 2.0 and 20 mm²), which can allow not only excellently, but also efficiently producing an article comprising a portion (10) provided with a hole(s) (13) externally opening, without using the above special tools such as needles or fingers.

[0027] A third aspect of the invention is the article according to the first aspect or the second aspect, wherein the section of the fiber (11) on the external face (12) is substantially circular and wherein its diameter is more than 1.5 mm, preferably between 1.5 and 10.0 mm, more preferably between 1.5 and 5.0 mm.

[0028] The expression “substantially” circular means each diameter of the fiber (11) is different from the average diameter of the fiber (11) by less than 10%, preferably at most 5%, by length per 100% by length of the average diameter.

[0029] A fourth aspect of the invention is the article according to any one of the first to the third aspects, wherein a difference between the curing temperature and the melting point of the thermoplastic resin is more than 10°C, preferably more than 20°C, more preferably more than 30°C, still more preferably at least 40°C.

[0030] A fifth aspect of the invention is the article according to any one of the first to the fourth aspects, wherein the thermoplastic resin exhibits a melting point of between 170 and 270 °C, preferably between 180 and 260 °C, more preferably between 190 and 250 °C, still more preferably from 195 to 245 °C.

[0031] A sixth aspect of the invention is the article according to any one of the first to the fifth aspects, wherein the thermoplastic resin is a thermoplastic resin dissolvable in a solvent.

[0032] Solubility in a solvent (it should be remembered that maximum weight of dissolved substance in the solvent at given one temperature and one pressure), for example water solubility in case of that the solvent is water, is one of basically well-known and constant physics (in particular, available in the “Handbooks of Chemistry and Physics”) of the compounds which are organic or inorganic. The person skilled art in the art understands that the solvent soluble resin can dissolve at least partly in the solvent. Preferably, the thermoplastic resin dissolvable in the solvent means the solubility of the thermoplastic resin in the solvent at 23 °C under a pressure equal to 1 atm is higher than 1 g/100ml, more preferably higher than 5 g/100ml, still more preferably higher than 10 g/100ml.

[0033] The solvent may be water, an organic solvent(s) (for example, alcohol, acetone and hexane), or combinations thereof, preferably, water, an alcohol(s) (for example,

methanol, ethanol and n-propanol) or combinations thereof.

[0034] A seventh aspect of the invention is the article according to the sixth aspect, wherein the thermoplastic resin is a water soluble thermoplastic resin.

[0035] An eighth aspect of the invention is the article according to any one of the first to the seventh aspects, wherein the thermoplastic resin is selected from the group consisting of polyethylene terephthalate, polybutylene terephthalate, polyvinylidene chloride, nylon 6, nylon 66, nylon 12, polyacetal, polyetherimide, polysulfone, polyvinyl alcohol and combinations thereof.

[0036] A ninth aspect of the invention is the article according to the eighth aspect, wherein the thermoplastic resin is polyvinyl alcohol, preferably poly butenediol-vinyl alcohol.

[0037] A tenth aspect of the invention is the article according to any one of the first to the ninth aspects, wherein the fiber (11) is made of monofilament, multifilament or combinations thereof, preferably monofilament or multifilament, more preferably monofilament.

[0038] An eleventh aspect of the invention is the article according to any one of the first to the tenth aspects, wherein the fiber (11) has an average length by number of less than 50 mm (for example, between 0 and 50 mm), preferably less than 40 mm (for example, between 1 and 40 mm).

[0039] The average length by number may be measured in accordance with JIS L 1015: 2010.

[0040] A twelfth aspect of the invention is the article according to any one of the first to the eleventh aspects, wherein the portion (10) is provided with a plurality of the fibers (11).

[0041] According to an preferable embodiment of the twelfth aspect, each of the fibers (11) has a cross sectional area on the external face (12), and each of the cross sectional areas is more than 1.0 mm² (for example, between 1.0 and 100.0 mm²), preferably more than 1.5 mm² (for example, between 1.5 and 60.0 mm²), more preferably more than 1.5 mm² (between 2.0 and 20.0 mm²).

[0042] A thirteenth aspect of the invention is the article according to the twelfth aspect, wherein the fibers (11) are arranged in substantially parallel to each other.

[0043] A fourteenth aspect of the invention is the article according to the twelfth aspect or the thirteenth aspect, wherein the fibers (11) are substantially uniformly distributed over the external face (12), that is, the cross sections of the fibers (11) are substantially uniformly distributed over the external face (12).

[0044] A fifteenth aspect of the invention is the article according to any of the first to the fourteenth aspects, wherein the article after curing is intended to come into contact with the ground.

[0045] A sixteenth aspect of the invention is the article according to the fifteenth aspect,

wherein the external face (12) forms an angle other than 0 degree with the surface of the ground, preferably the angle is from 10 to 90 degree, more preferably from 20 to 90 degree, still more preferably from 30 to 90 degree, particularly from 40 to 90 degree, more particularly from 50 to 90 degree, still more particularly from 60 to 90 degree, advantageously from 70 to 90 degree.

[0046] According to a preferred embodiment of the sixteenth aspect, the external face (12) is substantially perpendicular to the surface of the ground.

[0047] A seventeenth aspect of the invention is the article according to the fifteenth aspect or the sixteenth aspect, wherein the fiber(s) (11) extends substantially parallelly to the surface of the ground.

[0048] An eighteenth aspect of the invention is the article according to any one of the fifteenth to the seventeenth aspects, wherein the portion (10) is not intended to come into contact with the ground during the service life of the article.

[0049] According to a preferred embodiment of the eighteenth aspect, the article is a tire (1), and the portion (10) is an under-tread(s) of the tire (1).

[0050] A nineteenth aspect of the invention is the article according to any one of the fifteenth to the seventeenth aspects, wherein the portion (10) is not intended to come into contact with the ground during the service life of the article.

[0051] According to a preferred embodiment of the nineteenth aspect, the article is a tire (1), and the portion (10) is a tread block(s), a tread rib(s) or the both of the tire (1).

[0052] According to a preferred embodiment of the nineteenth aspect, the article is a tire (1), and the portion (10) is a cap-tread(s), a sub-tread(s) or the both of the tire (1), preferably a sub-tread(s) of the tire (1). The sub-tread(s) is positioned radially inner than the cap-tread(s) in the tire (1).

[0053] A twentieth aspect of the invention is the article according to the nineteenth aspect, wherein the portion (10) is that the rubber composition adjacent to the fiber(s) (11) is not intended to come into contact with the ground during the service life of the article.

[0054] In the eighteenth to the twentieth aspects, in case of that the article is a tire (1), the service life means the duration to use the tire (1) (for example, the term from the new state to the final state of the tire, the final state means a state on reaching the wear indicator bar(s) in the tread (2) of tire (1)).

[0055] A twenty first aspect of the invention is the article according to any one of the first to the twentieth aspects, wherein the article is a tire (1), a shoe, a conveyor or a caterpillar track.

[0056] According to a preferred embodiment of the twenty first aspect, the article is a shoe, preferably, the portion (10) is comprised of a shoe sole.

[0057] According to a preferred embodiment of the twenty first aspect, the article is a conveyor, preferably, the portion (10) is comprised of a conveyor belt.

- [0058] According to a preferred embodiment of the twenty first aspect, the article is a caterpillar track, preferably the portion (10) is comprised of a caterpillar track tread.
- [0059] A twenty second aspect of the invention is the article according to the twenty first aspect, wherein the article is a tire (1).
- [0060] According to a preferred embodiment of the twenty first aspect, the tire (1) is particularly intended to be equipped to passenger motor vehicles, including 4×4 (four-wheel drive) vehicles and SUV (Sport Utility Vehicles) vehicles, and also industrial vehicles in particular chosen from vans and heavy duty vehicles (i.e., bus or heavy road transport vehicles (lorries, tractors, trailers)).
- [0061] According to a preferred embodiment of the twenty second aspect, the portion (10) is a tread (2), a sidewall(s), an inner layer or combinations thereof, preferably a tread (2), a sidewall(s) or combinations thereof.
- [0062] A twenty third aspect of the invention is the article according to the twenty second aspect, wherein the fiber(s) (11) extends substantially parallelly to an axial direction of a tire (1).
- [0063] A twenty fourth aspect of the invention is the article according to the twenty second aspect, wherein the fiber(s) (11) extends substantially parallelly to a circumferential direction of a tire (1).
- [0064] A twenty fifth aspect of the invention is the article according to any one of the twenty second to the twenty fourth aspects, wherein the portion (10) is comprised of a tread (2) of a tire (1).
- [0065] According to a preferred embodiment of the twenty fifth aspect, the portion (10) is comprised of a cap-tread(s), a sub-tread(s), an under-tread(s) or combinations thereof, of a tread (2) of a tire (1), preferably a sub-tread(s), an under-tread(s) or the both, of a tread (2) of a tire (1), more preferably of an under-tread(s), of a tread (2) of a tire (1).

Brief Description of Drawings

- [0066] Other characteristics and advantages of the invention arise from the description made hereafter in reference to the annexed drawings which show, as nonrestrictive examples, of the embodiments of the object of the invention.
- [0067] In these drawings:
- [fig.1]Fig. 1 shows a schematic view of a cross sectional view of a portion (10) of an article according to the invention.
- [fig.2]Fig. 2 shows a schematic view of a cross sectional view of a cured portion (10c) of a cured article produced by a production method according to the invention, the production method comprising at least a step of removing fibers (11) from an article shown in Fig. 1 after curing the article.
- [fig.3]Fig. 3 shows a schematic view of a cross sectional view of a portion (10) of an

article according to the invention.

[fig.4]Fig. 4 shows a schematic view of a cross sectional view of a cured portion (10c) of a cured article produced by a production method according to the invention, the production method comprising at least a step of removing fibers (11) from an article shown in Fig. 3 after curing the article.

[0068] Each of the appended Figs. 1 to 4 schematically (in particular not to a specific scale) represents, in the cross section of the portion (10) of the article.

[0069] In the Fig. 1, the article is a tire (1) that comprises the portion (10) comprising a rubber composition. The portion (10) is an under-tread comprised of a tread (2) of the tire (1), the portion (10) is provided with a plurality of fibers (11) and an external face (12) forming an angle other than 0 degree with the surface of the ground. The fibers (11) pass through the portion (10), the fibers (11) are arranged in substantially parallel to each other, the fibers (11) extends substantially parallelly to the axial direction (A) and substantially perpendicularly to the radial direction (R) of the tire (1), each of the fibers (11) has a circular cross section having an area (s) and diameter (d) on the external face (12), and the circular cross sections of fibers (11) on the external face (12) are distributed at a substantially equal interval (t) over the external face (12). After curing the tire (1) at a curing temperature, the fibers (11) can remain in the portion (10) because the fibers (11) comprise a thermoplastic resin exhibiting a melting point higher than the curing temperature.

[0070] In the Fig. 2, the article is a cured tire (1c) that comprises the cured portion (10c) comprising a cured rubber composition. The cured portion (10c) is a cured under-tread comprised of a cured tread (2) of the cured tire (1c), the cured portion (10c) is provided with a plurality of a cured external face (12c) and holes (13), instead of the fibers (11) in Fig. 1. The holes (13) are formed by that the fibers (11) are removed from the tire (1) by applying an ultrasonic wave(s) to the tire (1), that is, to the fibers (11) with which the tire (1) is provided, after curing the tire (1) in Fig. 1.

[0071] In the Fig. 3, the article is a tire (1) that comprises the portion (10) comprising a rubber composition. The portion (10) is a sub-tread comprised of a tread block of a tread (2) of the tire (1), the portion (10) is provided with a plurality of fibers (11) and an external face (12) forming an angle other than 0 degree with the surface of the ground. The fibers (11) pass through the portion (10), the fibers (11) are arranged in substantially parallel to each other, the fibers (11) extends substantially parallelly to the circumferential direction (C) and substantially perpendicularly to the radial direction (R) of the tire (1), each of the fibers (11) has a circular cross section having an area (s) and a diameter (d) on the external face (12), and the circular cross sections of fibers (11) on the external face (12) are distributed at a substantially equal interval (t) over the external face (12). After curing the tire (1) at a curing temperature, the

fibers (11) can remain in the portion (10) because the fibers (11) comprise a thermoplastic resin exhibiting a melting point higher than the curing temperature.

[0072] In the Fig. 4, the article is a cured tire (1c) that comprises the cured portion (10c) comprising a cured rubber composition. The cured portion (10c) is a cured sub-tread comprised of a cured tread block of a cured tread (2c) of the cured tire (1), the cured portion (10c) is provided with a cured external face (12c) and a plurality of holes (13), instead of the fibers in Fig. 3. The holes (13) are formed by that the fibers (11) are removed from the tire (1) by applying an ultrasonic wave(s) to the tire (1), that is, to the fibers (11) with which the tire (1) is provided, after curing the tire (1) in Fig. 3.

[0073] Each of the Figs.1 to 4 shows, on the external face (12), a cross section of the portion (10) which forms a cuboid having a length (L: 25 mm), a width (W: 30 mm), and a thickness (T: 5 mm).

[0074] A twenty sixth aspect of the invention is the article according to any one of the first to twenty fifth aspects, wherein the rubber composition is based on an elastomer matrix.

[0075] Elastomer (or loosely “rubber”, the two terms being regarded as synonyms) of the “diene” type is to be understood in a known manner as an (meaning one or more) elastomer derived at least partly (i.e. a homopolymer or a copolymer) from diene monomers (monomers bearing two carbon-carbon double bonds, conjugated or not).

[0076] These diene elastomers can be classified into two categories: “essentially unsaturated” or “essentially saturated”. Generally, the expression “essentially unsaturated” is understood to mean a diene elastomer resulting at least in part from conjugated diene monomers having a content of units of diene origin (conjugated dienes) which is greater than 15% (mol %); thus it is that diene elastomers such as butyl rubbers or diene/ α -olefin copolymers of the EPDM type do not fall under the preceding definition and may especially be described as “essentially saturated” diene elastomers (low or very low content of units of diene origin, always less than 15%). In the category of “essentially unsaturated” diene elastomers, the expression “highly unsaturated” diene elastomer is understood to mean in particular a diene elastomer having a content of units of diene origin (conjugated dienes) which is greater than 50%.

[0077] Although it applies to any type of diene elastomer, a person skilled in the art of rubbers will understand that the invention is preferably employed with essentially unsaturated diene elastomers.

[0078] Given these definitions, the expression diene elastomer capable of being used in the compositions in accordance with the invention is understood in particular to mean:

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

(b) - any copolymer obtained by copolymerization of one or more conjugated dienes

with one another or with one or more vinyl aromatic compounds preferably having from 8 to 20 carbon atoms.

[0079] The following are suitable in particular as conjugated dienes: 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-di(C1-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 or 2-methyl-3-isopropyl-1,3-butadiene, an aryl-1,3-butadiene, 1,3-pentadiene or 2,4-hexadiene. The following, for example, are suitable as vinylaromatic compounds: styrene, ortho-, meta- or para-methylstyrene, the "vinyltoluene" commercial mixture, para-(tert-butyl) styrene, methoxystyrenes, chlorostyrenes, vinylmesitylene, divinylbenzene or vinylnaphthalene.

[0080] A twenty seventh aspect of the invention is the article according to the twenty sixth aspect, wherein the elastomer matrix comprises at least one diene elastomer selected from the group consisting of natural rubber (NR), synthetic polyisoprenes (IR), polybutadienes (BR), butadiene copolymers, isoprene copolymers and combinations thereof; such copolymers are preferably selected from the group consisting of butadiene copolymers combinations thereof, more preferably selected from the group consisting of styrene-butadiene copolymers (SBR), butadiene-isoprene copolymers (BIR), styrene-isoprene copolymers (SIR), styrene-butadiene-isoprene copolymers (SBIR) and combinations thereof, still more preferably selected from the group consisting of styrene-butadiene copolymers (SBR) and combinations thereof.

[0081] The diene elastomer may have any microstructure which depends on the polymerization conditions used, in particular on the presence or absence of a modifying agent, randomizing agent, or both and on the amounts of modifying agent, randomizing agent, or both employed. This elastomer may, for example, be a block, statistical, sequential or micro sequential elastomer and may be prepared in dispersion or in solution. This elastomer may be coupled, star-branched, or both; or else functionalized with a coupling, star-branching, or both; or functionalizing agent.

[0082] According to preferred embodiment of the twenty seventh aspect, the elastomer matrix comprises more than 50 phr (for example, more than 50 phr and up to 100 phr) of a first diene elastomer which is a styrene-butadiene copolymer, advantageously a solution styrene-butadiene copolymer, and optionally comprising less than 50 phr (for example, 0 phr to less than 50 phr) of a second diene elastomer which is different from the first diene elastomer.

[0083] According to a more preferred embodiment of the above preferred embodiment, the styrene-butadiene copolymer exhibits a styrene unit of less than 30% by weight (for example, between 3 and 30% by weight) per 100% by weight of the styrene-butadiene copolymer, preferably less than 27% by weight (for example, between 5 and 27% by weight), more preferably less than 23% by weight (for example, between 7 and 23% by

weight), still more preferably less than 20% by weight (for example, between 10 and 20% by weight), particularly at most 18% by weight (for example, from 12 to 18%). The styrene unit can be determined by ¹H NMR method in accordance with ISO 21561.

- [0084] According to a more preferred embodiment of the above preferred embodiment, the styrene-butadiene copolymer exhibits a glass transition temperature of less than -40°C (for example, between -40°C and -110°C), preferably less than -45°C (for example, between -45°C and -105°C), more preferably less than -50°C (for example, between -50°C and -100°C), still more preferably less than -55°C (for example, between -55°C and -95°C), particularly at most -60°C (for example, -60°C to -90°C).
- [0085] A twenty eighth aspect of the invention is the article according to any one of the first to the twenty seventh aspects, wherein the rubber composition is based on a reinforcing filler.
- [0086] In the twenty eighth aspect, the reinforcing filler may comprise a reinforcing organic filler (for example, carbon black), a reinforcing inorganic filler (for instance, silica) or combinations thereof.
- [0087] A twenty ninth aspect of the invention is the article according to the twenty eighth aspect, wherein the amount of reinforcing filler is more than 50 phr (for example, between 50 and 300 phr), preferably more than 60 phr (for example, between 60 and 280 phr), more preferably more than 70 phr (for example, between 70 and 260 phr), still more preferably more than 80 phr (for example, between 80 and 240 phr), particularly more than 90 phr (for example, between 90 and 220 phr), more particularly more than 100 phr (for example, between 100 and 200 phr), still more particularly more than 110 phr (for example, between 110 and 180 phr).
- [0088] Use may be made of any type of reinforcing filler known for its capabilities of reinforcing a rubber composition which can be used for the manufacture of tires, for example a reinforcing organic filler, such as carbon black, or a reinforcing inorganic filler, such as silica, with which a coupling agent is combined in a known way.
- [0089] As carbon blacks, all carbon blacks conventionally used in tires (“tire-grade” blacks) are suitable, such as for example reinforcing carbon blacks of the 100, 200 or 300 series in ASTM grades (such as for example, the N115, N134, N234, N326, N330, N339, N347 or N375 blacks), or carbon blacks higher series, the 500, 600, 700 or 800 series in ASTM grades (such as for example the N550, N660, N683, N772, N774 blacks). The carbon blacks might for example be already incorporated in an elastomer matrix, for instance, a diene elastomer, in the form of a masterbatch (see for example applications WO 97/36724 or WO 99/16600).
- [0090] The expression “reinforcing inorganic filler” should be understood here to mean any inorganic or mineral filler, whatever its color and its origin (natural or synthetic), also

referred to as “white filler”, “clear filler” or even “non-black filler”, in contrast to carbon black, capable of reinforcing by itself alone, without means other than an intermediate coupling agent, a rubber composition intended for the manufacture of tires, in other words capable of replacing, in its reinforcing role, a conventional tire-grade carbon black; such a filler is generally characterized, in a known manner, by the presence of hydroxyl (-OH) groups at its surface.

- [0091] The physical state under the presence of this filler is unimportant, whether it is in the form of powder, granules, beads or any other suitable densified form. Of course, the reinforcing inorganic filler of the mixtures of various reinforcing inorganic fillers, preferably of highly dispersible siliceous filler(s), aluminous filler(s), or both is described hereafter.
- [0092] Mineral fillers of the siliceous type (preferably silica (SiO_2)), the aluminous type (preferably alumina (Al_2O_3)), or combinations thereof are suitable in particular as the reinforcing inorganic fillers.
- [0093] A thirtieth aspect of the invention is the article according to the twenty eighth aspect or the twenty ninth aspect, wherein the reinforcing filler predominately comprises a reinforcing inorganic filler, that is, the reinforcing filler comprises more than 50% by weight of the reinforcing inorganic filler per 100% of the reinforcing filler, preferably the reinforcing filler comprises more than 60%, more preferably more than 70%, still more preferably more than 80%, particularly more than 90%, by weight of the reinforcing inorganic filler per 100% of the reinforcing filler.
- [0094] A thirty first aspect of the invention is the article according to the thirtieth aspect, wherein the reinforcing inorganic filler predominately comprises silica, that is, the reinforcing inorganic filler comprises more than 50% by weight of silica per 100% of the reinforcing inorganic filler, preferably the reinforcing inorganic filler comprises more than 60%, more preferably more than 70%, still more preferably more than 80%, particularly more than 90%, more particularly 100%, by weight of silica per 100% of the reinforcing inorganic filler.
- [0095] The silica may be a type of silica or a blend of several silicas. The silica used may be any reinforcing silica known to a person skilled in the art, in particular any precipitated or pyrogenic silica having a BET surface area and a CTAB specific surface area that are both less than 450 m^2/g , preferably from 20 to 400 m^2/g , more preferably 50 to 350 m^2/g , still more preferably 100 to 300 m^2/g , particularly between 150 and 250 m^2/g , wherein the BET surface area is measured according to a known method, that is, by gas adsorption using the Brunauer-Emmett-Teller method described in “The Journal of the American Chemical Society”, Vol. 60, page 309, February 1938, and more specifically, in accordance with the French standard NF ISO 9277 of December 1996 (multipoint volumetric method (5 points); where gas: nitrogen, degassing: 1 hour at

160°C, relative pressure range p/po: 0.05 to 0.17). The CTAB specific surface area is determined according to the French standard NF T 45-007 of November 1987 (method B). Such silica may be covered or not. Mention will be made, as low specific surface silica, of Sidistar R300 from Elkem Silicon Materials. Mention will be made, as highly dispersible precipitated silicas (“HDSs”), for example, of “Ultrasil 7000” and “Ultrasil 7005” from Evonik, “Zeosil 1165 MP”, “Zeosil 1135 MP” and “Zeosil 1115 MP” from Rhodia, “Hi-Sil EZ150G” from PPG, “Zeopol 8715”, “Zeopol 8745” and “Zeopol 8755” from Huber or the silicas with a high specific surface area as described in a patent application WO 03/016387. Mention will be made, as pyrogenic silicas, for example, of “CAB-O-SIL S-17D” from Cabot, “HDK T40” from Wacker, “Aeroperl 300/30”, “Aerosil 380”, “Aerosil 150” or “Aerosil 90” from Evonik. Such silica may be covered, for example, “CAB-O-SIL TS-530” covered with hexamethyldiasilazene or “CAB-O-SIL TS-622” covered with dimethyldichlorosilane from Cabot.

[0096] A person skilled in the art will understand that a reinforcing filler of another nature, in particular organic nature, such as carbon black, might be used as filler equivalent to the reinforcing inorganic filler described in the present section, provided that this reinforcing filler is covered with an inorganic layer, such as silica, or else comprises, at its surface, functional sites, in particular hydroxyls, requiring the use of a coupling agent in order to form the connection between the filler and the elastomer. By way of example, mention may be made of carbon blacks for tires, such as described in patent applications WO 96/37547 and WO 99/28380.

[0097] A thirty second aspect of the invention is the article according to any one of the twenty eighth to the thirty first aspects, wherein the reinforcing filler comprises less than 50 phr (for example, between 0 and 50 phr), preferably less than 40 phr (for example, between 0 and 40 phr), more preferably less than 30 phr (for example, between 0 and 30 phr), still more preferably less than 20 phr (for example, between 0 and 30 phr), particularly less than 15 phr (for example, between 1 and 15 phr), more particularly less than 10 phr (for example, between 2 and 10 phr), of carbon black.

[0098] Within each of the aforementioned ranges of content of carbon black in the rubber composition, there is a benefit of coloring properties (black pigmentation agent) and anti-UV properties of carbon blacks, without furthermore adversely affecting the typical performance provided by the reinforcing inorganic filler, namely high grip on wet ground, low hysteresis loss or both.

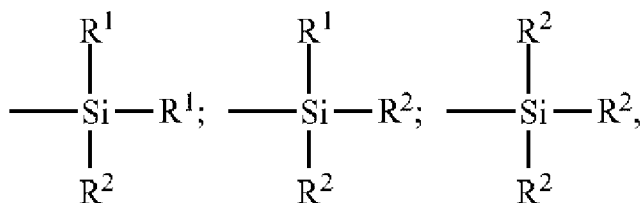
[0099] Use can be made in particular of silane polysulfides, referred to as “symmetrical” or “asymmetrical” depending on their particular structure, as described, for example, in applications WO 03/002648, WO 03/002649 and WO 2004/033548.

[0100] Particularly suitable silane polysulfides correspond to the following general formula (I):

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

- x is an integer from 2 to 8 (preferably from 2 to 5);
- A is a divalent hydrocarbon radical (preferably, C₁-C₁₈ alkylene groups or C₆-C₁₂ arylene groups, more particularly C₁-C₁₀, in particular C₁-C₄, alkenes, especially propylene);
- Z corresponds to one of the formulae below:

[Chem.1]



in which:

- the R¹ radicals which are unsubstituted or substituted and identical to or different from one another, represent a C₁-C₁₈ alkyl, C₅-C₁₈ cycloalkyl or C₆-C₁₈ aryl group (preferably, C₁-C₆ alkyl, cyclohexyl or phenyl groups, in particular C₁-C₄ alkyl groups, more particularly methyl, ethyl or both),
- the R² radicals which are unsubstituted or substituted and identical to or different from one another, represent a C₁-C₁₈ alkoxy or C₅-C₁₈ cycloalkoxy group (preferably a group selected from C₁-C₈ alkoxy and C₅-C₈ cycloalkoxy, more preferably a group selected from C₁-C₄ alkoxy, in particular methoxy and ethoxy), are suitable in particular, without limitation of the above definition.

[0101] In the case of a mixture of alkoxy silane polysulfides corresponding to the above formula (I), in particular normal commercially available mixtures, the mean value of the "x" indices is a fractional number preferably of between 2 and 5, more preferably of approximately 4. However, the invention can also advantageously be carried out, for example, with alkoxy silane disulfides (x = 2).

[0102] Mention will more particularly be made, as examples of silane polysulfides, of bis((C₁-C₄)alkoxy(C₁-C₄)alkylsilyl(C₁-C₄)alkyl)polysulfides (in particular disulfides, trisulfides or tetrasulfides), such as, for example, bis(3-trimethoxysilylpropyl) or bis(3-triethoxysilylpropyl)polysulfides. Use is in particular made, among these compounds, of bis(3-triethoxysilylpropyl)tetrasulfide, abbreviated to TESPT, of formula [(C₂H₅O)₃Si(CH₂)₃S₂]₂, or bis(3-triethoxysilylpropyl)disulfide, abbreviated to TESP, of formula [(C₂H₅SO)₃Si(CH₂)₃S]₂. Mention will also be made, as preferred examples, of bis(mono(C₁-C₄)alkoxydi(C₁-C₄)alkylsilylpropyl)polysulfides (in particular disulfides, trisulfides or tetrasulfides), more particularly bis(monoethoxydimethylsilylpropyl)tetrasulfide, as described in patent application WO 02/083782 (or US 7 217 751).

- [0103] Mention will in particular be made, as coupling agent other than alkoxy silane polysulfide, of bifunctional POSs (polyorganosiloxanes) or of hydroxysilane polysulfides ($R^2 = OH$ in the above formula (I)), such as described in patent applications WO 02/30939 (or US 6 774 255) and WO 02/31041 (or US 2004/051210), or of silanes or POSs carrying azodicarbonyl functional groups, such as described, for example, in patent applications WO 2006/125532, WO 2006/125533 and WO 2006/125534.
- [0104] As examples of other silane sulfides, mention will be made, for example, of the silanes bearing at least one thiol (-SH) function (referred to as mercaptosilanes), at least one blocked thiol function or both, such as described, for example, in patents or patent applications US 6 849 754, WO 99/09036, WO 2006/023815, WO 2007/098080, WO 2008/055986 and WO 2010/072685.
- [0105] Of course, use could also be made of mixtures of the coupling agents described previously, as described in particular in the aforementioned patent application WO 2006/125534.
- [0106] The content of coupling agent may be from 0.5 to 15% by weight per 100% by weight of the reinforcing inorganic filler, preferably silica.
- [0107] The amount of coupling agent may be less than 30 phr (for example, between 0.1 and 30 phr), preferably less than 25 phr (for example, between 0.5 and 25 phr), more preferably less than 20 phr (for example, between 1 and 20 phr).
- [0108] The rubber composition of the portion (10) of the article according to the invention may be based on all or a part(s) of the usual additives generally used in the elastomer compositions for articles (for example, tires, shoes, conveyor or caterpillar tracks), such as, for example, protection agents, such as antiozone waxes, chemical antiozonants, antioxidants, plasticizing agents, tackifying resins, methylene acceptors (for example phenolic novolak resin) or methylene donors (for example HMT or H3M hexamethylenetetramine (HMT) or hexamethoxymethylmelamine (H3M)), a crosslinking system based either on sulfur, or on donors of sulfur, or peroxide, or bismaleimides or combination thereof, vulcanization accelerators, or vulcanization activators.
- [0109] The rubber composition can be also based on coupling activators when a coupling agent is used, agents for covering the reinforcing inorganic filler or more generally processing aids capable, in a known way, by virtue of an improvement in the dispersion of the filler in the rubber matrix and of a lowering of the viscosity of the compositions, of improving their property of processing in the raw state; these agents are, for example, hydrolysable silanes, such as alkylalkoxysilanes, polyols, polyethers, amines, or hydroxylated or hydrolysable polyorganosiloxanes.
- [0110] A thirty third aspect of the invention is the article according to any one of the first to the thirty second aspects, wherein the rubber composition is based on no blowing agent

or based on less than 5 phr, preferably less than 2 phr, more preferably less than 1 phr, still more preferably less than 0.5 phr, particularly less than 0.1 phr, of a blowing agent. The blowing agent is a compound which can decompose thermally and which is intended to release, during thermal activation, for example during the vulcanization of the article (for example a tire), a large amount of gas and to thus result in the formation of bubbles. The blowing agent is preferably selected from a group of compounds consisting of: azo, nitroso, hydrazine, carbazide, semicarbazide, tetrazole, carbonate, citrate, and combinations thereof.

[0111] The rubber composition of the portion (10) of the article according to the invention may be manufactured in appropriate mixers using two successive preparation phases well known to a person skilled in the art: a first phase of thermomechanical working or kneading (referred to as “non-productive” phase) at high temperature, up to a maximum temperature of between 110°C and 190°C, preferably between 130°C and 180°C, followed by a second phase of mechanical working (referred to as “productive” phase) at a lower temperature, typically of less than 110°C, for example between 40°C and 100°C, finishing phase during which the crosslinking or vulcanization system is incorporated.

[0112] A process which can be used for the manufacture of such compositions comprises, for example and preferably, the following steps:

- incorporating in the elastomer matrix, for instance, the diene elastomer(s), in a mixer, the reinforcing filler, during a first stage (“non productive” stage) everything being kneaded thermomechanically (for example in one or more steps) until a maximum temperature of between 110°C and 190°C is reached;
- cooling the combined mixture to a temperature of less than 100°C;
- subsequently incorporating, during a second stage (referred to as a "productive" stage), a crosslinking system;
- kneading everything up to a maximum temperature of less than 110°C.

[0113] According to a preferred embodiment of the invention, the first (non-productive) phase is carried out in a single thermomechanical stage during which all the necessary constituents may be introduced into an appropriate mixer, such as a standard internal mixer, followed, in a second step, for example after kneading for 1 to 2 minutes, by the other additives, optional additional filler-covering agents or processing aids, with the exception of the crosslinking system. The total kneading time, in this non-productive phase, is preferably between 1 and 15 min.

[0114] The crosslinking system is preferably based on sulfur and on a primary vulcanization accelerator, in particular on an accelerator of sulfenamide type. Added to this vulcanization system are various known secondary accelerators or vulcanization activators, such as zinc oxide, stearic acid, guanidine derivatives (in particular diphenyl-

guanidine), and the like, incorporated during the first non-productive phase, during the productive phase or both. The content of sulfur is preferably between 0.5 and 10.0 phr, more preferably between 0.5 and 3.0 phr, and that of the primary accelerator is preferably between 0.5 and 5.0 phr.

- [0115] Use may be made, as accelerator (primary or secondary) of any compound capable of acting as accelerator of the vulcanization of elastomer matrix, for instance, diene elastomers, in the presence of sulfur, in particular accelerators of the thiazoles type and their derivatives, accelerators of thiurams types, or zinc dithiocarbamates. These accelerators are more preferably selected from the group consisting of 2-mercaptobenzothiazyl disulfide (abbreviated to "MBTS"), N-cyclohexyl-2-benzothiazole sulfenamide (abbreviated to "CBS"), N,N-dicyclohexyl-2-benzothiazolesulfenamide ("DCBS"), N-tert-butyl-2-benzothiazolesulfenamide ("TBBS"), N-tert-butyl-2-benzothiazolesulfenimide ("TBSI"), zinc dibenzylthiocarbamate ("ZBEC"), Tetrabenzylthiuram disulfide ("TBZTD") and combinations thereof.
- [0116] The fiber(s) (11) of the portion (10) of the article according to the invention is embedded in the rubber composition obtained in the above, and the rubber composition with the fiber(s) (11) is subsequently calendered, for example in the form of a sheet or of a plaque, in particular for laboratory characterization, or else extruded in the form of a rubber profiled element which can be used directly as a part of a portion (10) of an article, for example, a tire tread (2), a shoe sole, a conveyor belt and a caterpillar track tread. Each of the tip(s) of the fiber(s) (11) appears on a surface of the sheet or the plaque (as the external face (12) of the portion (10) of the article according to the invention), that is, each of the fiber(s) (11) has a cross section on the surface of the sheet or the plaque.
- [0117] The curing (or vulcanization) is carried out at a temperature lower than a melting point of a thermoplastic resin which the fiber(s) (11) comprises, in order to prevent the thermoplastic resin from melting during the vulcanization.
- [0118] A thirty fourth aspect of the invention is a production method of a cured article, comprising at least a step of removing a fiber(s) (11) from an article according to any one of the first to thirty third aspects by an ultrasonic wave(s) after curing the article comprising a portion (10) comprising a rubber composition at a curing temperature, the portion (10) provided with at least one external face (12) and the fiber(s) (11) passing through the portion (10), the fiber (11) comprising a thermoplastic resin exhibiting a melting point higher than the curing temperature, and the fiber(s) (11) having a cross sectional area on the external face (12).
- [0119] The thermoplastic resin comprised of the fiber(s) (11) with which the article is provided can be melted by applying the ultrasonic wave(s) to the article.

- [0120] A thirty fifth aspect of the invention is the production method according to the thirty fourth aspect, wherein the thermoplastic resin is a thermoplastic resin dissolvable in a solvent.
- [0121] A thirty sixth aspect of the invention is the production method according to the thirty fifth aspect, wherein the step of removing the fiber(s) (11) from the article by the ultrasonic wave(s) occurs in the solvent.
- [0122] The thermoplastic resin can be dissolved in the solvent, and it can flow out from the cross section on the external face (12).
- [0123] A thirty seventh aspect of the invention is the production method according to the thirty fifth aspect or the thirty sixth aspect, wherein the solvent is water, methanol, ethanol n-propanol or combinations thereof, preferably water.
- [0124] A thirty eighth aspect of the invention is the production method according to any one of the thirty fifth to the thirty seventh aspect, wherein the solvent has a temperature of at least room temperature (for example, 23 °C), preferably between 50 and 90 °C.
- [0125] A thirty ninth aspect of the invention is the production method according to any one of the thirty fourth to the thirty eighth aspects, wherein the ultrasonic wave(s) has a frequency of more than 20 kHz, preferably between 25 and 100 kHz.
- [0126] The invention relates to the rubber compositions and the above articles, both in the mixed state (after mixing and before curing) and in the cured state (i.e., after crosslinking or vulcanization) unless expressly stated otherwise.
- [0127] Each of the above aspects including each of the preferred range(s), matter(s) or combinations thereof may be applied to any one of the other aspects or the embodiments of the invention.
- [0128] The invention is further illustrated by the following non-limiting examples.

Example

- [0129] Three specimens (identified as T-1 and T-2 (examples according to invention), and T-3 (a comparative example)) comprising a rubber composition were tested. Each of the examples according to invention (T-1 and T-2) can be a portion (10) of an article according to the invention. The formulation of the rubber composition with the content of the various products expressed in phr is given at Table 1.
- [0130] Each rubber composition was produced as follows: The reinforcing filler, the, the elastomer matrix and the various other ingredients, with the exception of sulfur and a sulfenamide type vulcanization accelerator (as a vulcanization accelerator) in the crosslinking system, were successively introduced into an internal mixer having an initial vessel temperature of approximately 60°C; the mixer was thus approximately 70% full (% by volume). Thermomechanical working (non-productive phase) was then carried out in one stage, which lasts in total approximately 3 to 4 minutes, until a maximum “dropping” temperature of 165°C was reached. The mixture thus obtained

was recovered and cooled and then sulfur and the sulfenamide type vulcanization accelerator were incorporated on an external mixer (homofinisher) at 20 to 30°C, everything being mixed (productive phase) for an appropriate time (for example, between 5 and 12 min).

[0131] The rubber compositions thus obtained were subsequently calendered, either in the form of sheets (thickness of 1 to 3 mm) or of fine sheets of rubber, for the measurement of their physical or mechanical properties, or in the form of profiled elements which could be used directly, after cutting, assembling or both to the desired dimensions, for example as tire semi-finished products, in particular as tire treads (2).

[0132] After molding into the form of sheets made of each of these rubber compositions and before the following test measurements, the sheets were stacked with arranging a plurality of the following thermoplastic fibers (the thermoplastic fibers means the fibers predominately comprising the thermoplastic resin, that is, the fibers comprising more than 50% by weight of thermoplastic resin per 100% by weight of the fibers) in parallel to each other at each equal interval over each of the sheets to form a laminated cuboid:

- T-1: Polyvinyl alcohol fiber (cross section area on the external face (12): 2.4 mm², diameter: 1.75 mm, length: 30 mm, amount by weight of poly butenediol vinyl alcohol per 100% by weight of the fiber: more than 99 %, melting point of polyvinyl alcohol: 200 °C, monofilament, produced by Nippon Synthetic Chemical Industry Co-operation);

- T-2: Polyvinyl alcohol fiber (cross section area on the external face (12): 4.9 mm², diameter: 2.5 mm, length: 30 mm, amount by weight of polyvinyl alcohol per 100% by weight of the fiber: more than 94%, melting point of polyvinyl alcohol: 200 °C, multifilament, twisted 3/3/3/4 construction with C40/1 (150dtex) produced by Kuraray Co., Ltd);

- T-3: Polypropylene fiber (cross section area on the external face (12): 19.6 mm², diameter: 5 mm, length: 30 mm, melting point of polypropylene: 160 °C, string twisted fiber with PP rope produced by Otsuka Cooperation).

[0133] Each of the laminated cubic was placed in a press with heated platens at a temperature (typically 160 °C), for the time that was necessary for the crosslinking of each of these rubber compositions (typically 25 minutes), at a pressure (typically 16 bar).

[0134] Then, each of the specimens (T-1 and T-2, except T-3) described in the Fig. 1 or Fig. 2 was obtained, and the thermoplastic fibers extended to the direction of the width of the cuboid, and had both tips being in contact with air.

[0135] The other specimen (T-3) could not be obtained such cuboid described in the Fig. 1 or Fig. 2 because the thermoplastic fibers were melted, and the space was filled in the rubber composition during the above curing.

[0136] Subsequently, an ultrasonic wave (the frequency: 42 kHz) generated from an ultrasonic generator (SUS-100, produced by Shimadzu Cooperation) was applied to each of the specimens (T-1, T-2 and T-3) for 16 hours in a water bath, that is, a container of water heated (as a solvent) to a given temperature (from 60 to 80 °C), in order to remove the thermoplastic fibers from each of the specimens.

[0137] Finally, the two specimens (T-1 and T-2) described in the Fig. 3 or Fig. 4 were obtained, and they had a plurality of holes(s) (13) extending in the direction of the width of the cuboid instead of the above thermoplastic fibers, opposite ends of each of the holes (13) opening outside.

[0138] [Table 1]

SBR (1) [phr]	100
Carbon black (2) [phr]	4
Silica (3) [phr]	110
Coupling agent (4) [phr]	11
Liquid plasticizer (5) [phr]	10
Hydrocarbon resin (6) [phr]	65
Antioxidant (7) [phr]	4.4
Antiozone wax [phr]	2.6
DPG (8) [phr]	2.4
Stearic acid [phr]	3
Zinc oxide [phr]	0.9
Sulphur [phr]	0.9
CBS (9) [phr]	2.3

- (1) SBR: Solution SBR with 16% of styrene unit ($T_{gDSC} = -65$ °C);
- (2) Carbon black: Carbon black (ASTM grade N234 from Cabot);
- (3) Silica: Silica (“Zeosil 1165MP” from Rhodia (CTAB, BET: 160 m²/g));
- (4) Coupling agent TESPT (“Si69” from Evonik);
- (5) Oleic sunflower oil (“Agripure 80” from Cargill, Weight percent oleic acid: 100%);
- (6) Cycloaliphatic hydrocarbon resins (“ESCOREZ5600” from ExxonMobil, $T_{gDSC} = 52$ °C);
- (7) Mixture of N-(1,3-dimethylbutyl)-N-phenyl-para-phenylenediamine (“Santoflex 6-PPD” from Flexsys) and 2,2,4-trimethyl-1,2-dihydroquinolone (“TMQ” from Lanxess);
- (8) Diphenylguanidine (“Perkacit DPG” from Flexsys);
- (9) N-dicyclohexyl-2-benzothiazolesulfenamide (“Santocure CBS” from Flexsys).

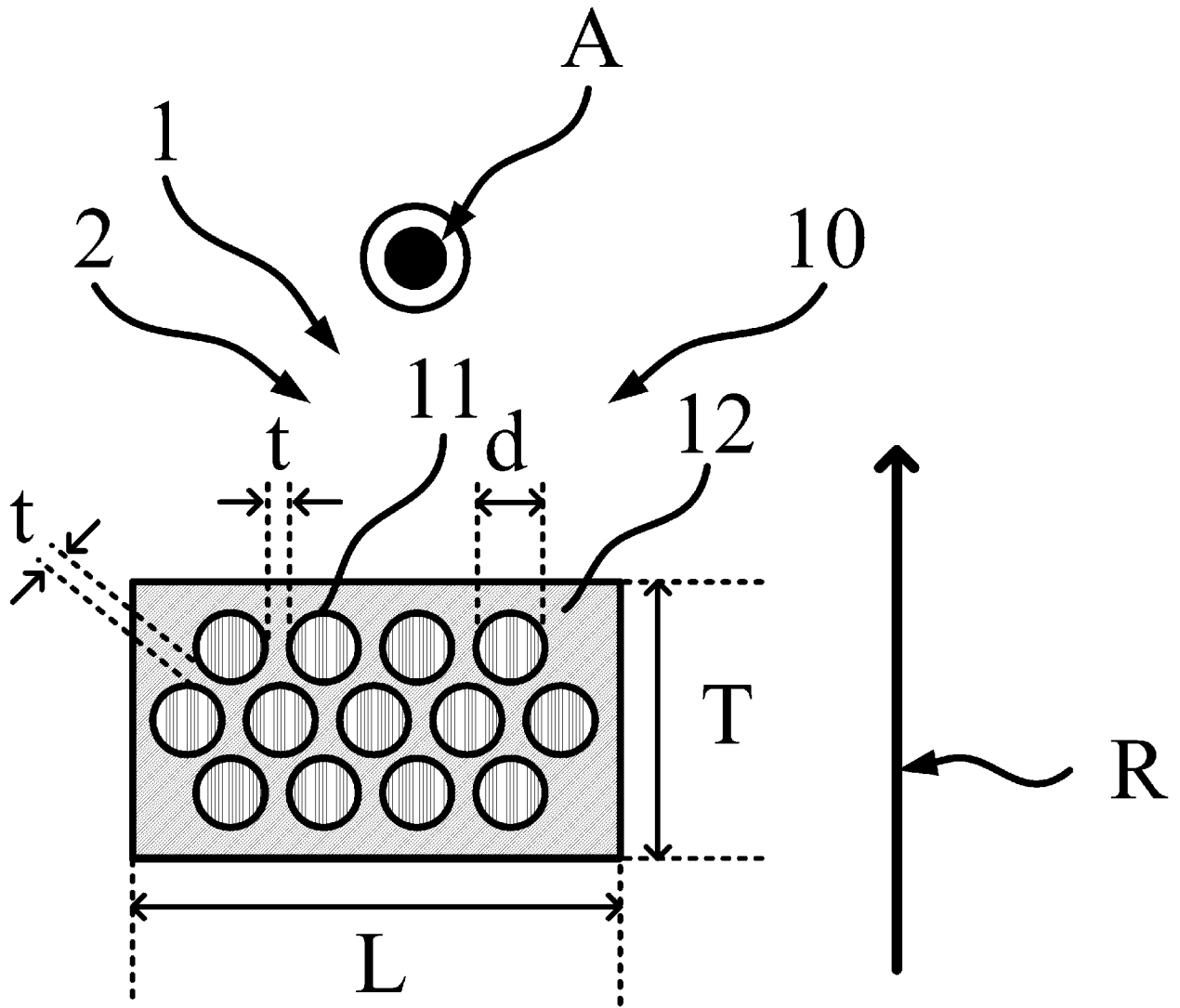
Claims

- [Claim 1] An article comprising a portion (10) comprising a rubber composition cured or intended to be cured at a curing temperature;
the portion (10) provided with at least one external face (12) and at least one fiber (11) passing through the portion (10);
the fiber (11) comprising a thermoplastic resin exhibiting a melting point higher than the curing temperature; and
the fiber (11) having a cross sectional area (s) on the external face (12).
- [Claim 2] The article according to Claim 1, wherein the cross sectional area (s) of the fiber (11) on the external face (12) is more than 1.0 mm².
- [Claim 3] The article according to Claim 1 or Claim 2, wherein the section of the fiber (11) on the external face (12) is substantially circular and wherein its diameter is more than 1.5 mm.
- [Claim 4] The article according to any one of Claims 1 to 3, wherein a difference between the curing temperature and the melting point of the thermoplastic resin is more than 10°C.
- [Claim 5] The article according to any one of Claims 1 to 4, wherein the thermoplastic resin exhibits a melting point of between 170 and 270 °C.
- [Claim 6] The article according to any one of Claims 1 to 5, wherein the thermoplastic resin is a thermoplastic resin dissolvable in a solvent.
- [Claim 7] The article according to Claim 6, wherein the thermoplastic resin is a water soluble thermoplastic resin.
- [Claim 8] The article according to any one of Claims 1 to 7, wherein the thermoplastic resin is selected from the group consisting of polyethylene terephthalate, polybutylene terephthalate, polyvinylidene chloride, nylon 6, nylon 66, nylon 12, polyacetal, polyetherimide, polysulfone, polyvinyl alcohol and combinations thereof.
- [Claim 9] The article according to Claim 8, wherein the thermoplastic resin is polyvinyl alcohol.
- [Claim 10] The article according to any one of Claims 1 to 9, wherein the fiber (11) is made of monofilament, multifilament or combinations thereof.
- [Claim 11] The article according to any one of Claims 1 to 10, wherein the fiber (11) has an average length by number of less than 50 mm.
- [Claim 12] The article according to any one of Claims 1 to 11, wherein the portion (10) is provided with a plurality of the fibers (11).
- [Claim 13] The article according to Claim 12, wherein the fibers (11) are arranged in substantially parallel to each other.

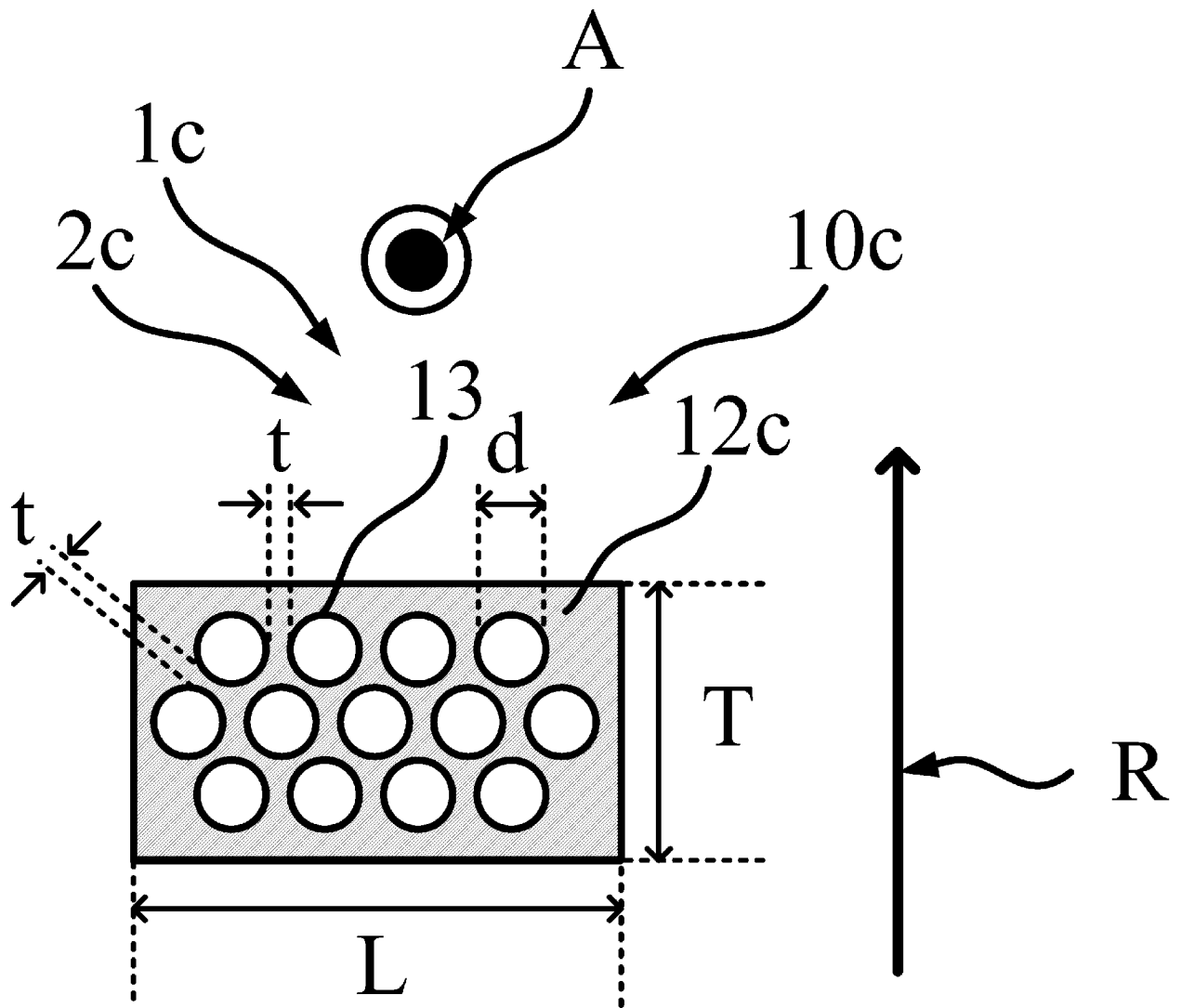
- [Claim 14] The article according to Claim 12 or Claim 13, wherein the fibers (11) are substantially uniformly distributed over the external face (12).
- [Claim 15] The article according to any one of Claims 1 to 14, wherein the article after curing is intended to come into contact with the ground.
- [Claim 16] The article according to Claim 15, wherein the external face (12) forms an angle other than 0 degree with the surface of the ground.
- [Claim 17] The article according to Claim 15 or Claim 16, wherein the fiber(s) (11) extends substantially parallelly to the surface of the ground.
- [Claim 18] The article according to any one of Claims 15 to 17, wherein the portion (10) is not intended to come into contact with the ground during the service life of the article.
- [Claim 19] The article according to any one of Claims 15 to 17, wherein the portion (10) is intended to come into contact with the ground during the service life of the article.
- [Claim 20] The article according to Claim 19, wherein the portion (10) is that the rubber composition adjacent to the fiber(s) (11) is not intended to come into contact with the ground during the service life of the article.
- [Claim 21] The article according to any one of Claims 1 to 20, wherein the article is a tire (1), a shoe, a conveyor or a caterpillar track.
- [Claim 22] The article according to Claim 21, wherein the article is a tire (1).
- [Claim 23] The article according to Claim 22, wherein the fiber(s) (11) extends substantially parallelly to an axial direction of a tire (1).
- [Claim 24] The article according to Claim 22, wherein the fiber(s) (11) extends substantially parallelly to a circumferential direction of a tire (1).
- [Claim 25] The article according to any one of Claims 22 to 24, wherein the portion (10) is comprised of a tread (2) of a tire (1).
- [Claim 26] The article according to any one of Claims 1 to 25, wherein the rubber composition is based on an elastomer matrix.
- [Claim 27] The article according to Claim 26, wherein the elastomer matrix comprises at least one diene elastomer selected from the group consisting of natural rubber, synthetic polyisoprenes, polybutadienes, butadiene copolymers, isoprene copolymers and combinations thereof.
- [Claim 28] The article according to any one of Claims 1 to 27, wherein the rubber composition is based on a reinforcing filler.
- [Claim 29] The article according to Claim 28, wherein the amount of reinforcing filler is more than 50 phr.
- [Claim 30] The article according to Claim 28 or Claim 29, wherein the reinforcing filler predominately comprises a reinforcing inorganic filler.

- [Claim 31] The article according to Claim 30, wherein the reinforcing inorganic filler predominately comprises silica.
- [Claim 32] The article according to any one of Claims 28 to 31, wherein the reinforcing filler comprises less than 50 phr of carbon black.
- [Claim 33] The article according to any one of Claims 1 to 32, wherein the rubber composition is based on no blowing agent or based on less than 5 phr, preferably less than 2 phr, more preferably less than 1 phr, still more preferably less than 0.5 phr, particularly less than 0.1 phr, of a blowing agent.
- [Claim 34] A production method of a cured article, comprising at least a step of removing a fiber(s) (11) from an article according to any one of Claims 1 to 33 by an ultrasonic wave(s) after curing the article (1) comprising a portion (10) comprising a rubber composition at a curing temperature, the portion (10) provided with at least one external face (12) and the fiber(s) (11) passing through the portion (10), the fiber (11) comprising a thermoplastic resin exhibiting a melting point higher than the curing temperature, and the fiber(s) (11) having a cross sectional area on the external face (12).
- [Claim 35] The production method according to Claim 34, wherein the thermoplastic resin is a thermoplastic resin dissolvable in a solvent.
- [Claim 36] The production method according to Claim 35, wherein the step of removing the fiber(s) (11) from the article by the ultrasonic wave(s) occurs in the solvent.
- [Claim 37] The method according to Claim 35 or Claim 36, wherein the solvent is water, methanol, ethanol n-propanol or combinations thereof.
- [Claim 38] The production method according to any one of Claims 35 to 37, wherein the solvent has a temperature of at least room temperature.
- [Claim 39] The production method according to any one of Claims 34 to 38, wherein the ultrasonic wave(s) has a frequency of more than 20 kHz.

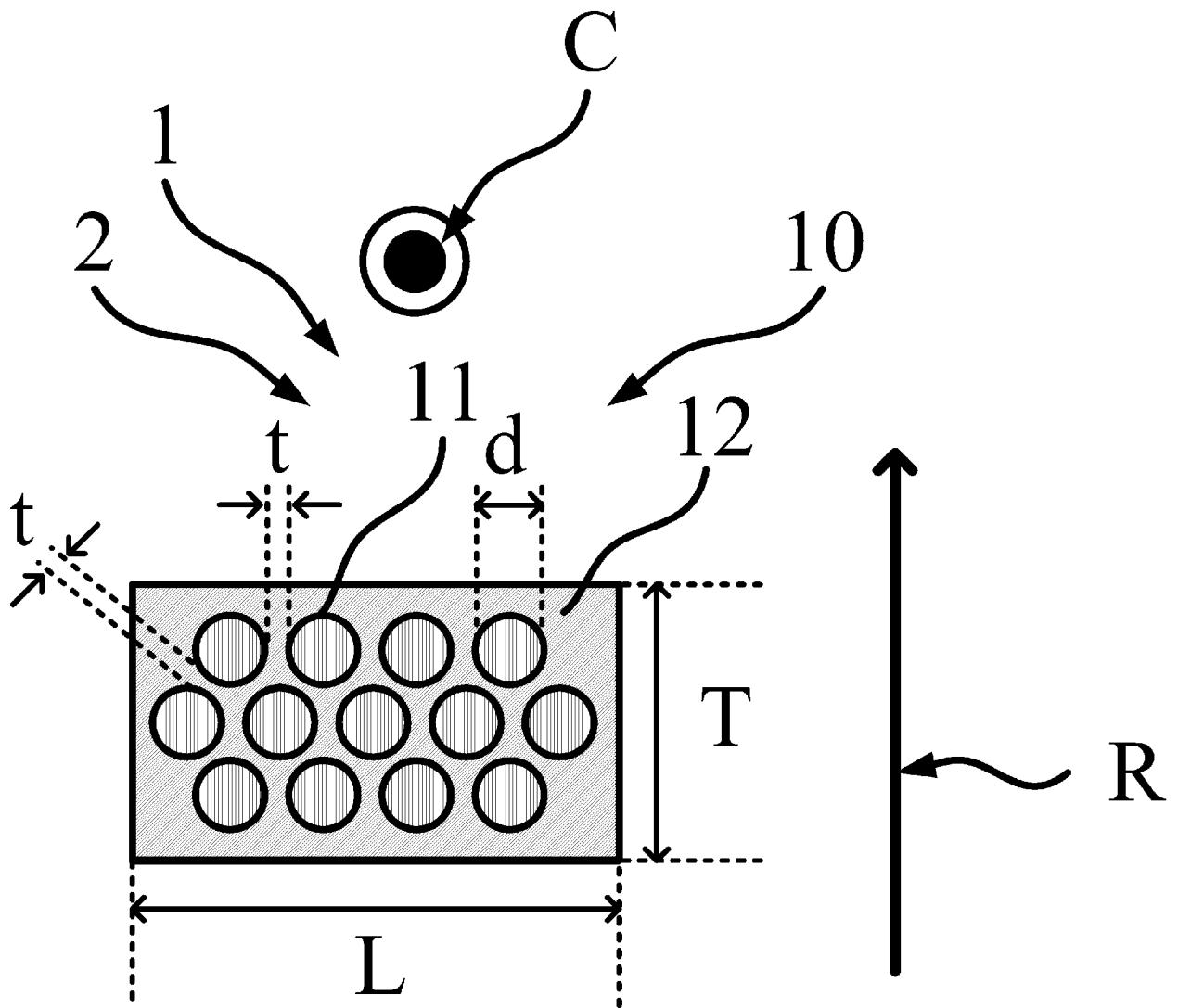
[Fig. 1]



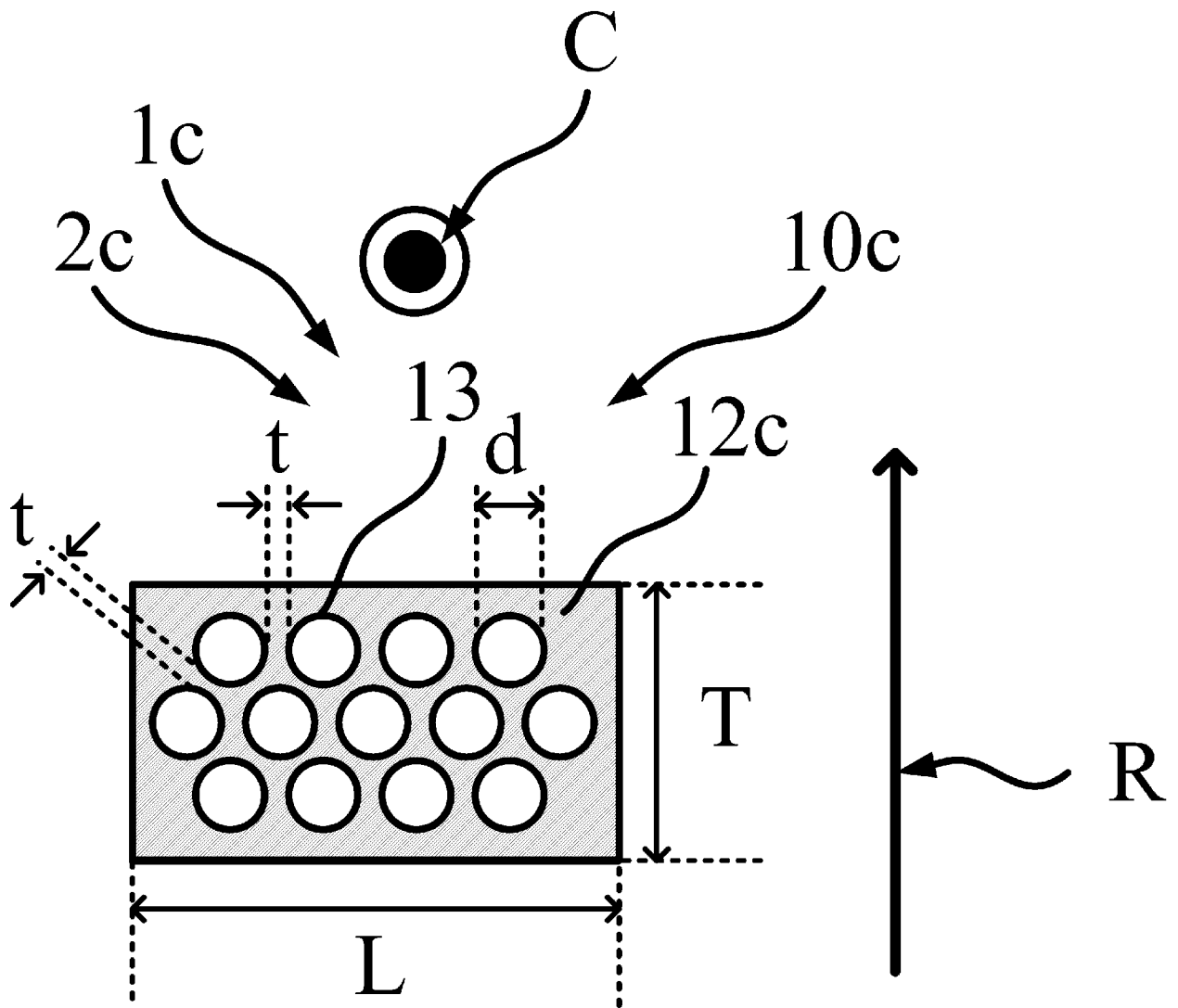
[Fig. 2]



[Fig. 3]



[Fig. 4]



INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2019/043795

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	B29D30/66	B60C1/00	B29D29/08	B29D35/12	
ADD.	B29K21/00	B29K29/00	B29K67/00	B29K77/00	B29K105/12
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) B29D B60C B29K

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 practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	paragraphs [0018] - [0020], [0025], [0041], [0046], [0059], [0062]; figures	11-20, 27-33
A		34-39
X	EP 2 916 034 A1 (MITSUBOSHI BELTING LTD [JP]) 9 September 2015 (2015-09-09)	1,5-10, 21,26,27
Y	paragraphs [0020], [0039]; figures	2-4, 11-20, 22-33
A		34-39
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :	"T" 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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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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"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search 24 January 2020	Date of mailing of the international search report 31/01/2020
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Kopp, Christian
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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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Y	paragraphs [0059], [0061]; figures	14-19, 22-33
A		34-39
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