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(54) Title: A LAMINATE

(57) Abstract: A laminate comprises at least three superposed portions comprising a first portion being made of a first rubber composition (FC), a second portion being made of a second rubber composition (SC) and a third portion being made of a third rubber composition (TC), the second portion being arranged between the first portion and the third portion; wherein each of the rubber compositions is based on at least an elastomer matrix, and more than 65 phr of a reinforcing filler; wherein the average glass transition temperature of elastomer matrix in the first rubber composition (FC) is lower than that in the second rubber composition (SC); and wherein the average glass transition temperature of elastomer matrix in the second rubber composition (SC) is higher than that in the third rubber composition (TC).

Description

Title of Invention: A LAMINATE

Technical Field

[0001] The field of the invention is that of laminates intended in particular for rubber articles, in more particular for tires, in still more particular for treads of tires, in especial for treads of tires capable of rolling over ground surface covered with snow.

[0002] As is known, the snow tires classified in a category of use "snow", identified by an inscription the alpine symbol ("3-peak-mountain with snowflake"), marked on their sidewalls, mean tires whose tread patterns, tread compounds and/or structures are primarily designed to achieve, in snow conditions, a performance better than that of normal tires intended for normal on-road use with regard to their abilities to initiate, maintain or stop vehicle motion.

Citation List

Patent Literature

[0003] PTL 1: WO 2012/069565

[0004] Snowy ground has a feature of having a low friction coefficient and a constant objective of manufacturers of rubber articles is improvement of a grip performance of rubber articles on snow-covered (snowy) ground during the service life of the rubber articles.

Summary of Invention

Technical Problem

[0005] During the research, the inventor has discovered that a specific laminate with rubber compositions intended in particular for a rubber article, for example, a tire tread, which allows an unexpectedly improved grip performance on snowy ground in the new state and in the worn state.

[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 Tg_{DSC} (glass transition temperature) is measured in a known way by DSC (Differential Scanning Calorimetry) in accordance with 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, the product of the reaction of the various constituents used, or both; some of the constituents being able, intended, or both, to react together, at least partly, during the various manufacturing phases of the composition, in particular during the vulcanization (curing).

Solution to Problem

[0012] A first aspect of the invention is a laminate comprising at least three superposed portions comprising a first portion being made of a first rubber composition (FC), a second portion being made of a second rubber composition (SC) and a third portion being made of a third rubber composition (TC), the second portion being arranged between the first portion and the third portion, wherein each of the rubber compositions is based on at least an elastomer matrix, and more than 65 phr of a reinforcing filler, wherein the average glass transition temperature of elastomer matrix in the first rubber composition (FC) is lower than that in the second rubber composition (SC), and wherein the average glass transition temperature of elastomer matrix in the second rubber composition (SC) is higher than that in the third rubber composition (TC).

[0013] The average glass transition temperature is calculated by FOX equation ($(Tg_{DSC\ Average}+273)^{-1}=\Sigma(w_i/100/(Tg_{DSC\ i}+273))$, $Tg_{DSC\ Average}$: Average glass transition temperature, w_i: Amount in phr of the i^{th} elastomer, $Tg_{DSC\ i}$: Glass transition temperature in °C of the i^{th} elastomer).

Advantageous Effects of Invention

[0014] The specific laminate with the rubber compositions allows an unexpectedly improved grip performance on snowy ground in the new state and in the worn state.

[0015] Each of the below aspect(s), the embodiment(s), the instantiation(s), and the variant(s) including each of the preferred range(s), matter(s), or combinations thereof may be applied to any one of the other aspect(s), the other embodiment(s), the other instantiation(s) and the other variant(s) of the invention unless expressly stated otherwise.

[0016] Each of the rubber compositions (FC, SC and TC) of the laminate according to the invention is based on each elastomer matrix.

[0017] 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).

[0018] 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%.

[0019] Although it applies to any type of diene elastomer, a person skilled in the art of rubber products (for example, tires) will understand that the invention is preferably employed with essentially unsaturated diene elastomers.

[0020] 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.

[0021] The following are suitable in particular as conjugated dienes: 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-di(C_1-C_5 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.

[0022] A second aspect of the invention is the laminate according to the first aspect, wherein each of the rubber compositions is such that the elastomer matrix comprises at least one diene elastomer selected from the group consisting of polybutadienes (BR), natural rubber (NR), synthetic polyisoprenes (IR), butadiene copolymers, and isoprene copolymers, and combinations thereof.

[0023] According to a preferred embodiment of the second aspect, at least one of the rubber compositions, especially each of the rubber compositions, is such that the copolymers are preferably selected from the group consisting of butadiene copolymers, and 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.

[0024] 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.

[0025] According to a more preferred embodiment of the preferred embodiment, at least one of the first rubber composition (FC) or the third rubber composition (TC), especially each of the first rubber composition (FC) and the third rubber composition (TC), is such that the elastomer matrix comprises more than 50 phr and up to 100 phr, preferably 55 to 95 phr, more preferably 60 to 90 phr, still more preferably 65 to 85 phr, particularly 70 to 80 phr, of a first diene elastomer which is a styrene butadiene rubber, especially a solution styrene butadiene rubber, as a styrene butadiene copolymer, and the elastomer matrix comprises no second diene elastomer or comprises less than 50 phr, preferably 5 to 45 phr, more preferably 10 to 40 phr, still more preferably 15 to 35 phr, particularly 20 to 30 phr, of a second diene elastomer which is different from the first diene elastomer.

[0026] According to a still more preferred embodiment of the more preferred embodiment, at least one of the first rubber composition (FC) or the third rubber composition (TC), especially each of the first rubber composition (FC) and the third rubber composition (TC), is such that the first diene elastomer exhibits a glass transition temperature (Tg_{DSC}) 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).

[0027] According to a particular embodiment of the more preferred embodiment or the still more preferred embodiment, at least one of the first rubber composition (FC) or the third rubber composition (TC), especially each of the first rubber composition (FC) and the third rubber composition (TC), is such that the second diene elastomer is a polybutadiene(s) (BR) more preferably having a content (molar %) of 1,2-units of between 4% and 80% or those having a content (molar %) of cis-1,4-units of greater than 80%, more preferably greater than 90% (molar %), still more preferably greater

than or equal to 96% (molar %).

[0028] According to a more particular embodiment of the more preferred embodiment, the still more preferred embodiment or the particular embodiment, at least one of the first rubber composition (FC) or the third rubber composition (TC), especially each of the first rubber composition (FC) and the third rubber composition (TC), is such that 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.

[0029] A third aspect of the invention is the laminate according to the first aspect or the second aspect, wherein the second rubber composition (SC) is such that the elastomer matrix comprises more than 50 phr and up to 100 phr, preferably 60 to 100 phr, more preferably 70 to 100 phr, still more preferably 80 to 100 phr, particularly 90 to 100 phr, more particularly 100 phr, of a first diene elastomer which is a styrene butadiene rubber, especially a solution styrene butadiene rubber, as a styrene butadiene copolymer, and the elastomer matrix comprises no second diene elastomer or comprises less than 50 phr, preferably less than 40 phr, more preferably less than 30 phr, still more preferably less than 20 phr, particularly less than 10 phr, of a second diene elastomer which is different from the first diene elastomer.

[0030] A fourth aspect of the invention is the laminate according to any one of the first to the third aspects, wherein the second rubber composition (SC) is such that the average glass transition temperature of elastomer matrix is more than -65°C, preferably more than -60°C, more preferably more than -55°C, still more preferably more than -50°C, particularly more than -45°C, more particularly more than -40°C, still more particularly more than -35°C, advantageously more than -30°C.

[0031] According to a preferred embodiment of the invention, the second rubber composition (SC) is such that the average glass transition temperature of elastomer matrix is less than 0°C, preferably less than -5°C, more preferably less than -10°C, still more preferably less than -15°C, particularly less than -20°C.

[0032] A fifth aspect of the invention is the laminate according to any one of the first to the fourth aspects, wherein each of the first rubber composition (FC) and the third rubber composition (TC) is such that the average glass transition temperature of elastomer matrix is at most -40°C, preferably at most -45°C, more preferably at most -50°C, still more preferably at most -55°C, particularly more than -60°C, more particularly at most

-65°C, still more particularly at most -70°C, advantageously at most -75°C.

[0033] According to a preferred embodiment of the invention, each of the first rubber composition (FC) and the third rubber composition (TC) is such that the average glass transition temperature of elastomer matrix is at least -120°C, preferably at least -115°C, more preferably at least -110°C, still more preferably at least -105°C, particularly at least -100°C, more particularly at least -95°C, still more particularly at least -90°C, advantageously at least -85°C.

[0034] Each of the rubber compositions (FC, SC and TC) of the laminate according to the invention is based on more than 65 phr of a reinforcing filler.

[0035] 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 the rubber article, 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.

[0036] Each of the rubber compositions is such that the reinforcing filler may comprise at least one of carbon black or a reinforcing inorganic filler (preferably, silica).

[0037] A sixth aspect of the invention is the laminate according to any one of the first to the fifth aspects, wherein each of the rubber compositions is such that 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% by weight 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% by weight of the reinforcing filler.

[0038] 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.

[0039] The physical state under the presence of this filler is unimportant, whether it is in the form of powder, microbeads, 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.

[0040] 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.

[0041] According to a preferred embodiment of the sixth aspect, the reinforcing inorganic filler predominately comprises silica, that is, the reinforcing inorganic filler comprises more than 50% by weight of silica per 100% by weight 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% by weight of the reinforcing inorganic filler.

[0042] 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.

[0043] 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 rubber articles (for example, tires), such as described in patent applications WO 96/37547 and WO 99/28380.

[0044] 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.

[0045] Particularly suitable silane polysulfides correspond to the following general formula (I):

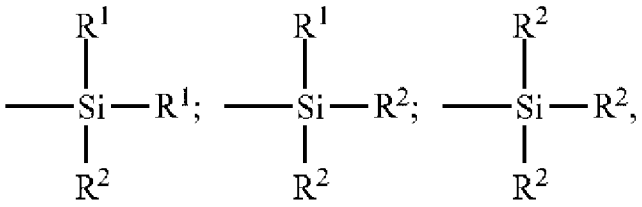
(I) Z - A - Sx - A - Z , in which:

- x is an integer from 2 to 8 (preferably from 2 to 5);
- A is a divalent hydrocarbon radical (preferably, C_1-C_{18} alkylene groups or C_6-C_{12}

arylene groups, more particularly C_1-C_{10}, in particular C_1-C_4, alkylenes, especially propylene);

- Z corresponds to one of the formulae below:

[Chem.1]



in which:

- the R^1 radicals which are unsubstituted or substituted and identical to or different from one another, represent a C_1-C_{18} alkyl, C_5-C_{18} cycloalkyl or C_6-C_{18} aryl group (preferably, C_1-C_6 alkyl, cyclohexyl or phenyl groups, in particular C_1-C_4 alkyl groups, more particularly methyl, ethyl, or both),
- the R^2 radicals which are unsubstituted or substituted and identical to or different from one another, represent a C_1-C_{18} alkoxyl or C_5-C_{18} cycloalkoxyl group (preferably a group selected from C_1-C_8 alkoxyls and C_5-C_8 cycloalkoxyls, more preferably a group selected from C_1-C_4 alkoxyls, in particular methoxyl and ethoxyl), are suitable in particular, without limitation of the above definition.

[0046] In the case of a mixture of alkoxysilane 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 alkoxysilane disulfides (x = 2).

[0047] Mention will more particularly be made, as examples of silane polysulfides, of bis((C$_1$-C$_4$)alkoxyl(C$_1$-C$_4$)alkylsilyl(C$_1$-C$_4$)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 $[(C_2H_5O)_3Si(CH_2)_3S_2]_2$, or bis(3-triethoxysilylpropyl)disulfide, abbreviated to TESPD, of formula $[(C_2HSO)_3Si(CH_2)_3S]_2$. Mention will also be made, as preferred examples, of bis(mono(C$_1$-C$_4$)alkoxyldi(C$_1$-C$_4$)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).

[0048] Mention will in particular be made, as coupling agent other than alkoxysilane 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.

[0049] 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.

[0050] 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.

[0051] According to a preferred embodiment of the invention, each of the rubber compositions comprises a reinforcing inorganic filler (preferably silica), and a coupling agent of which the amount is from 0.5 to 15% by weight per 100% by weight of the reinforcing inorganic filler (preferably silica).

[0052] According to a preferred embodiment of the invention, each of the rubber compositions comprises a reinforcing inorganic filler (preferably silica), and a coupling agent of which the amount is 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), still more preferably less than 15 phr (for example, between 1.5 and 15 phr).

[0053] A seventh aspect of the invention is the laminate according to any one of the first to the sixth aspects, wherein each of the rubber compositions is such that the reinforcing filler comprises less than 65 phr, preferably less than 60 phr, more preferably less than 55 phr, still more preferably less than 50 phr, particularly less than 45 phr, more particularly less than 40 phr, still more particularly less than 35 phr, advantageously less than 30 phr, more advantageously less than 25 phr, still more advantageously less than 20 phr, especially less than 15 phr, more especially less than 10 phr, still more especially less than 5 phr, of carbon black.

[0054] Within each of the aforementioned ranges of content of carbon black in the rubber compositions (FC, SC and TC), 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 low hysteresis loss.

[0055] According to a preferred embodiment of the seventh aspect, each of the rubber compositions is such that the reinforcing filler comprises more than 0 phr of carbon black.

[0056] An eighth aspect of the invention is the laminate according to any one of the first to

the seventh aspects, wherein each of the rubber compositions is such that the amount of reinforcing filler is more than 70 phr, preferably more than 75 phr, more preferably more than 80 phr, still more preferably more than 85 phr, particularly more than 90 phr, more particularly more than 95 phr, still more particularly more than 100 phr.

[0057] According to a preferred embodiment of the invention, each of the rubber compositions is such that the amount of reinforcing filler is less than 300 phr, preferably less than 250 phr, more preferably less than 200 phr.

[0058] A ninth aspect of the invention is the laminate according to any one of the first to the eighth aspects, wherein the amount in phr of the reinforcing filler in the first rubber composition (FC) is higher than that in the second rubber composition (SC), and wherein the amount in phr of the reinforcing filler in the second rubber composition (SC) is lower than that in the third rubber composition (TC).

[0059] According to a preferred embodiment of the ninth aspect, the second rubber composition (SC) is such that the amount of reinforcing filler is less than 120 phr, preferably less than 110 phr.

[0060] According to a preferred embodiment of the ninth aspect, each of the first rubber composition (FC) and the third rubber composition (TC) is such that the amount of reinforcing filler is at least 110 phr, preferably at least 120 phr.

[0061] Each of the rubber compositions (FC, SC and TC) of the laminate in according to the invention may be based on all or a portion(s) of the usual additives generally used in the elastomer compositions intended for manufacture of rubber articles (for example, tires), such as, for example, protection agents, such as antiozone waxes, chemical antiozonants, antioxidants, plasticizing agent (for example, liquid plasticizer(s), hydrocarbon resin(s)), tackifying resins, methylene acceptors (for example, phenolic novolak resin) or methylene donors (for example, hexamethylenetetramine (HMT) or hexamethoxymethylmelamine (H3M)), a crosslinking system, or combinations thereof.

[0062] Each of the rubber compositions (FC, SC and TC) of the laminate in according to the invention 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.

[0063] A tenth aspect of the invention is the laminate according to any one of the first to the ninth aspects, wherein each of the rubber compositions is further based on a plasticizing agent, preferably wherein the amount of plasticizing agent is more than 50 phr, more preferably more than 60 phr, still more preferably more than 70 phr, particularly

more than 80 phr, in order to soften each of the rubber compositions by diluting the elastomer matrix and the reinforcing filler.

[0064] The plasticizing agent may comprise at least one of a liquid plasticizer or a hydrocarbon resin. At ambient temperature (20°C) under atmosphere pressure, the liquid plasticizer is liquid, and the hydrocarbon resin is solid.

[0065] Each of the rubber compositions (FC, SC and TC) of the laminate 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 sulfur and the vulcanization accelerator in the crosslinking system are incorporated.

[0066] A process which can be used for the manufacture of each of such compositions (FC, SC and TC) comprises, for example and preferably, the following steps:

- incorporating in the elastomer matrix, in a mixer, the reinforcing filler during a first stage (referred to as a "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), sulfur and the vulcanization accelerator in the crosslinking system; and
- kneading everything up to a maximum temperature of less than 110°C.

[0067] By way of example, the first (non-productive) phase is carried out in a single thermomechanical stage during which all the necessary constituents are 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 sulfur and the vulcanization accelerator in the crosslinking system. The total kneading time, in this non-productive phase, is preferably between 1 and 15 min.

[0068] After cooling the mixture thus obtained, sulfur and the vulcanization accelerator in the crosslinking system are then incorporated at low temperature (for example, between 40°C and 100°C), generally in an external mixer, such as an open mill; the combined mixture is then mixed (the second (productive) phase) for a few minutes, for example between 2 and 15 min.

[0069] An eleventh aspect of the invention is the laminate according to any one of the first to the tenth aspects, wherein each of the rubber compositions is further based on a

crosslinking system.

[0070] According to a preferred embodiment of the eleventh aspect, the crosslinking system is based on at least one peroxide.

[0071] According to a preferred embodiment of the eleventh aspect, the crosslinking system is based on at least one bismaleimide.

[0072] According to a preferred embodiment of the eleventh aspect, the crosslinking system is based on at least one vulcanization accelerator other than sulfur-based vulcanization accelerator. The vulcanization accelerator other than sulfur-based vulcanization accelerator may promote a vulcanization reaction in the rubber composition. The vulcanization accelerator other than sulfur-based vulcanization accelerator may be based on guanidine derivatives (in particular diphenylguanidine), or combinations thereof.

[0073] According to a preferred embodiment of the eleventh aspect, the crosslinking system is based on at least one vulcanization activator. The vulcanization activator can increase the efficiency of the vulcanization accelerators, and may be based on zinc (pure zinc, zinc derivatives (for example, zinc fatty acid salt), or combinations thereof), fatty acid (in particular, stearic acid), or combinations thereof.

[0074] A twelfth aspect of the invention is the laminate according to the eleventh aspect, wherein the crosslinking system is based on sulfur, wherein the amount in phr of sulfur in the first rubber composition (FC) is lower than that in the second rubber composition (SC), and wherein the amount in phr of sulfur in the second rubber composition (SC) is higher than that in the third rubber composition (TC).

[0075] The sulfur in the crosslinking (or vulcanization) system is to say vulcanization sulfur which may be sulfur, sulfur derived from a sulfur-donating agent, or combinations thereof.

[0076] According to a preferred embodiment of the twelfth aspect, the amount of sulfur in the first rubber composition (FC) is less than 1.8 phr, preferably less than 1.6 phr, the amount of sulfur in the second rubber composition (SC) is more than 1.4 phr, preferably at least 1.6 phr, and the amount of sulfur in the third rubber composition (TC) is less than 1.8 phr, preferably less than 1.6 phr.

[0077] According to a preferred embodiment of the twelfth aspect, each of the rubber compositions is such that the amount of sulfur is less than 10 phr.

[0078] A thirteenth aspect of the invention is the laminate according to the eleventh aspect, wherein the crosslinking system is based on at least one sulfur-based vulcanization accelerator, wherein the amount in phr of sulfur-based vulcanization accelerator in the first rubber composition (FC) is lower than that in the second rubber composition (SC), and wherein the amount in phr of sulfur-based vulcanization accelerator in the second rubber composition (SC) is higher than that in the third rubber composition (TC).

[0079] The sulfur-based vulcanization accelerator is a vulcanization accelerator comprising

at least one sulfur atom in a molecule. The sulfur-based vulcanization accelerator may promote the sulfur vulcanization reaction in the rubber compositions.

[0080] According to a preferred embodiment of the thirteenth aspect, sulfur-based vulcanization accelerator is based on sulfenamide type vulcanization accelerator(s) (for example, N-Cyclohexyl-2-benzothiazolesulfenamide (CBS), N-tert-Butyl-2-benzothiazolesulfenamide (TBBS), 2-(Morpholinothio)benzothiazole (MBS), N,N-Dicyclohexyl-2-benzothiazolesulfenamide (DCBS), N-Tert-Butyl-2-benzothiazolesulfenamide (TBSI)), thiazole type vulcanization accelerator(s) (for example, 2,2'-Dithiobisbenzothiazole (MBTS), Zinc 2-mercaptobenzothiazole (ZMBT)), thiourea type vulcanization accelerator(s), thiuram type vulcanization acclerator(s) (for example, Tetrabenzylthiuram disulfide (TBzTD)), dithiocarbamate type vulcanization accelerator(s) (for example, Zinc ethylphenyldithiocarbamate (ZEPC), Zinc dibenzyldithiocarbamate (ZDBzC)), or combinations thereof.

[0081] According to a preferred embodiment of the thirteenth aspect, the amount of sulfur-based vulcanization accelerator in the first rubber composition (FC) is less than 2.0 phr, preferably less than 1.8 phr, the amount of sulfur in the second rubber composition (SC) is more than 1.6 phr, preferably at least 1.8 phr, and the amount of sulfur-based vulcanization accelerator in the third rubber composition (TC) is less than 2.0 phr, preferably less than 1.8 phr.

[0082] According to a preferred embodiment of the thirteenth aspect, each of the rubber compositions is such that the amount of sulfur-based vulcanization accelerator is less than 10 phr.

[0083] Each of the final compositions thus obtained is subsequently extruded or 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 laminate or a rubber article, for example, a tire tread.

[0084] As for making the laminate according to the invention, it is possible to build a first layer of a homogeneous rubber composition, as the first rubber composition (FC), a second layer of a homogeneous rubber composition, as the second rubber composition (SC), and a third layer of a homogeneous rubber composition, as the third rubber composition (TC), then to superpose the second layer onto the third layer and next to superpose the first layer onto the second layer, or sandwich the other layer(s) or portion(s) between these layers (between the first layer and the second layer or between the second layer and the third layer), to get the laminate.

[0085] According to a preferred embodiment of the invention, the second portion is adjacent to at least one of the first portion or the third portion, preferably the second portion is adjacent to the first portion and the third portion.

[0086] A preferred embodiment of the invention is an article comprising a laminate according to the invention.

[0087] According to a more preferred embodiment of the preferred embodiment, the article is intended to contact with the ground.

[0088] According to a still more preferred embodiment of the more preferred embodiment, the first portion (or the third portion) is arranged nearer to the ground than the second portion which is arranged near to the ground than the third portion (or the first portion). In case of that the article is a tire, the superposed portions which are the first portion, the second portion and the third portion are radially superposed portions, that is, the first portion (or the third portion) is radially exterior to the second portion which is radially exterior to the third portion (or the first portion).

[0089] The "radially" means "in the radial direction" which is a direction perpendicular to the axis of the rotation of a tire.

[0090] According to a particular embodiment of the more preferred embodiment or the still more preferred embodiment, at least one of the first portion, the second portion or the third portion, preferably each of the portions, is intended to come into contact with the ground during the service life of article.

[0091] The service life means the duration to use the article (for example, the term from the new state to the final state of the article, in case of that the article is a tire, the final state means a state on reaching the wear indicator bar(s) in the tread of tire).

[0092] According to a more particular embodiment of the preferred embodiment, the more preferred embodiment, the still more preferred embodiment or the particular embodiment, the article is a tire (for example, a tire tread), a shoe (for example, a shoe sole), a conveyor (for example, a conveyor belt) or a caterpillar track (a caterpillar track tread), preferably a tire, a shoe or a caterpillar track, more preferably a tire tread, a shoe sole or a caterpillar track tread, still more preferably a tire tread.

[0093] According to a still more particular embodiment of the preferred embodiment, the more preferred embodiment, the still more preferred embodiment, the particular embodiment or the more particular embodiment, the article is a tire comprising several tire parts which are a tread intended to at least partially contact with the ground, two sidewalls intended to contact with the outside air, but not to contact with the ground, two beads, a crown prolonged by two sidewalls ended by two beads, a carcass reinforcement formed at least one ply reinforced by radial textile cards, the carcass reinforcement passing into the crown and the sidewalls and the carcass reinforcement anchored in the two beads, preferably further comprising crown reinforcement placed between carcass reinforcement and the tread, more preferably further comprising an inner liner intended to protect the carcass reinforcement from diffusion of air coming from a space inside the tire, and the inner liner placed radially inner than carcass rein-

forcement.

[0094] According to an advantageously embodiment of the still more particular embodiment, the laminate according to any one of the first to the thirteenth aspect is placed in at least one of the above tire parts, between two of the above tire parts, radially outer than one of the above tire parts, radially inner than one of the above tire parts, or combinations thereof.

[0095] A fourteenth aspect of the invention is a tire comprising a laminate according to any one of the first to the thirteenth aspects.

[0096] A fifteenth aspect of the invention is the tire according to the fourteenth aspect, wherein the tire comprises a tread comprising a laminate according to any one of the first to the thirteenth aspects.

[0097] According to a preferred embodiment of the fourteenth aspect or the fifteenth aspect, the tire is a snow tire.

[0098] According to a more preferred embodiment of the fourteenth aspect, the fifteenth aspect or the preferred embodiment, the tires are particularly intended to equip passenger motor vehicles, including 4×4 (four-wheel drive) vehicles and SUV (Sport Utility Vehicles) vehicles, and industrial vehicles particularly selected from vans and heavy duty vehicles (i.e., bus or heavy road transport vehicles (lorries, tractors, trailers)).

[0099] The vulcanization (or curing) is carried out in a known way at a temperature generally of between 110°C and 190°C for a sufficient time which can vary, for example, between 5 and 90 min depending in particular on the curing temperature, the vulcanization system adopted and the vulcanization kinetics of the composition(s) under consideration.

[0100] The invention relates to the rubber composition(s), to the laminate(s), to the article(s), to the tire (s) and the tire tread(s) described above, both in the raw state (i.e., before curing) and in the cured state (i.e., after crosslinking or vulcanization).

[0101] The invention is further illustrated by the following non-limiting examples.

Example

[0102] In order to confirm the effect of the invention, three rubber compositions (C-1, C-2 and C-3) were used. The rubber compositions are based on a diene elastomer (a blend of SBR and BR or SBR only) reinforced with a blend of silica and carbon black (as a reinforcing filler). The formulations of the rubber compositions are shown in Table 1 with the amount of the various products expressed in phr. Each average glass transition temperature of elastomer is also shown in Table 1.

[0103] Each rubber composition was produced as follows: The reinforcing filler, the elastomer matrix and the various other ingredients, with the exception of sulfur and 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).

[0104] The rubber compositions thus obtained were subsequently calendered, either in the form of sheets (thickness of 2 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.

[0105] In order to confirm the effect of the invention, three tires (T-1: a reference, T-2 and T-3: examples according to the invention) having treads comprising laminates comprising a radially external portion being made of a first rubber composition, a radially intermediate portion being made of a second rubber composition and a radially internal portion being made of a second rubber composition, the radially intermediate portion being adjacent to the radially externally and internally portions, the laminate being produced by superposition of the sheets of the rubber compositions (C-1, C-2, C-3 or combinations thereof) respectively which are the first rubber composition, the second rubber composition or the third rubber composition, as shown in Table 2, are compared.

[0106] These tires, as snow tires having treads comprising grooves circumferentially, axially, or both extending, were conventionally manufactured and in all respects identical apart from the rubber compositions and the laminates of the tire treads. These tires are radial carcass passenger vehicle tires and the size of them is 245/40R18.

[0107] As snow grip measurements, a 1,400 cc passenger car provided on all of the four wheels with the same kind of these tires (in the new state) under 270 kPa (front tires) or 250 kPa (rear tires) of tire inflation pressure mounted onto 7.5Jx18 rim was run on a snow covered road at a temperature of -10 °C, the deceleration from 50 to 5 km/h during sudden longitudinal braking while anti-lock braking system (ABS) activated was measured. The above snow grip measurements were conducted on a hard pack snow with a CTI penetrometer reading of about 90 in accordance with Standard ASTM F1805.

[0108] Further, all of the tires were fitted to the front and rear axles of motor vehicles, under nominal tire inflation pressure, and were subjected to rolling on a circuit in order to reproduce the tires in the worn state. Then, the above snow grip measurements were

done with the worn tires. Each of the worn tires was still in the service life, and in each of them, each radially internal portion made of each second rubber composition at least partially appeared on each tread surface and could at least partially contact with the ground.

[0109] The results of the snow grip measurements are reported in Table 2, in relative units, the base 100 being selected for the reference T-1 (it should be remembered that a value of greater than 100 indicates an improved performance).

[0110] The results from Table 2 demonstrate that the examples T-2 and T-3 according to the invention have certainly higher values of the snow grip performance than that of the reference T-1 in the new state and the worn state.

[0111] In conclusion, the laminate according to the invention allows an unexpectedly improved grip performance on snowy ground in the new state and in the worn state.

[0112] [Table 1]

	C-1	C-2	C-3
BR (1)	25		
SBR1 (2)	75		
SBR2 (3)		100	100
Carbon black (4)	4	4	4
Silica (5)	120	100	100
Coupling agent (6)	9.6	8	8
Plasticizing agent (7)	81	81	81
Antioxidant (8)	5.7	5.7	5.7
Antiozone wax	2.7	2.7	2.7
DPG (9)	2.1	2.1	2.1
Stearic acid	3	3	3
Zinc oxide	1.5	1.5	1.5
Sulphur	1.4	1.8	4.0
Vulcanization accelerator (10)	1.6	2.0	4.6
Average glass transition temperature of elastomer (°C)	-77	-25	-25

(1) BR with 0.3% of 1,2 vinyl; 2.7% of trans; 97% of cis-1,4 (Tg_{DSC} = -105°C);

(2) Solution SBR with 16% of styrene unit and 24% of unit 1,2 of the butadiene part (Tg_{DSC} = -65°C);

(3) Solution SBR with 41% of styrene unit and 24% of unit 1,2 of the butadiene part (Tg_{DSC} = -25°C);

(4) Carbon black (ASTM grade N234 from Cabot);

(5) Silica ("Zeosil 1165MP" from Rhodia (CTAB, BET: about 160 m^2/g));

(6) Coupling agent TESPT ("Si69" from Evonik);

(7) Combination of Oleic sunflower oil ("Agripure 80" from Cargill, Weight percent oleic acid: 100%) and Hydrocarbon resin C5/C9 type ("Escorez ECR-373" from Exxon, Tg_{DSC}= 44°C);

(8) Combination 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);

(9) Diphenylguanidine ("Perkacit DPG" from Flexsys);

(10) N-dicyclohexyl-2-benzothiazolesulfenamide ("Santocure CBS" from Flexsys).

[0113] [Table 2]

	C-1	C-2	C-3
First rubber composition (FC)	C-1	C-1	C-1
Second rubber composition (SC)	C-1	C-2	C-3
Third rubber composition (TC)	C-1	C-1	C-1
Snow grip in the new state	100	104	103
Snow grip in the worn state	100	106	104

Claims

[Claim 1] A laminate comprising at least three superposed portions comprising a first portion being made of a first rubber composition (FC), a second portion being made of a second rubber composition (SC) and a third portion being made of a third rubber composition (TC), the second portion being arranged between the first portion and the third portion; wherein each of the rubber compositions is based on at least:
- an elastomer matrix; and
- more than 65 phr of a reinforcing filler;
wherein the average glass transition temperature of elastomer matrix in the first rubber composition (FC) is lower than that in the second rubber composition (SC), and wherein the average glass transition temperature of elastomer matrix in the second rubber composition (SC) is higher than that in the third rubber composition (TC).

[Claim 2] The laminate according to Claim 1, wherein each of the rubber compositions is such that the elastomer matrix comprises at least one diene elastomer selected from the group consisting of polybutadienes, natural rubber, synthetic polyisoprenes, butadiene copolymers, isoprene copolymers, and combinations thereof.

[Claim 3] The laminate according to Claim 1 or Claim 2, wherein the second rubber composition (SC) is such that the elastomer matrix comprises more than 50 phr and up to 100 phr of a first diene elastomer which is a styrene butadiene rubber, and the elastomer matrix comprises no second diene elastomer or comprises less than 50 phr of a second diene elastomer which is different from the first diene elastomer.

[Claim 4] The laminate according to any one of Claims 1 to 3, wherein the second rubber composition (SC) is such that the average glass transition temperature of elastomer matrix is more than -65°C.

[Claim 5] The laminate according to any one of Claims 1 to 4, wherein each of the first rubber composition (FC) and the third rubber composition (TC) is such that the average glass transition temperature of elastomer matrix is at most -40°C.

[Claim 6] The laminate according to any one of Claims 1 to 5, wherein each of the rubber compositions is such that the reinforcing filler predominately comprises a reinforcing inorganic filler, preferably wherein the reinforcing inorganic filler predominately comprises silica.

[Claim 7] The laminate according to any one of Claims 1 to 6, wherein each of

the rubber compositions is such that the reinforcing filler comprises less than 65 phr of carbon black.

[Claim 8] The laminate according to any one of Claims 1 to 7, wherein each of the rubber compositions is such that the amount of reinforcing filler is more than 70 phr.

[Claim 9] The laminate according to any one of Claims 1 to 8, wherein the amount in phr of the reinforcing filler in the first rubber composition (FC) is higher than that in the second rubber composition (SC), and wherein the amount in phr of the reinforcing filler in the second rubber composition (SC) is lower than that in the third rubber composition (TC).

[Claim 10] The laminate according to any one of Claims 1 to 9, wherein each of the rubber compositions is further based on more than 60 phr of a plasticizing agent.

[Claim 11] The laminate according to any one of Claims 1 to 10, wherein each of the rubber compositions is further based on a crosslinking system.

[Claim 12] The laminate according to Claim 11, wherein the crosslinking system is based on sulfur, wherein the amount in phr of sulfur in the first rubber composition (FC) is lower than that in the second rubber composition (SC), and wherein the amount in phr of sulfur in the second rubber composition (SC) is higher than that in the third rubber composition (TC).

[Claim 13] The laminate according to Claim 11, wherein the crosslinking system is based on a sulfur-based vulcanization accelerator, wherein the amount in phr of sulfur-based vulcanization accelerator in the first rubber composition (FC) is lower than that in the second rubber composition (SC), and wherein the amount in phr of sulfur-based vulcanization accelerator in the second rubber composition (SC) is higher than that in the third rubber composition (TC).

[Claim 14] A tire comprising a laminate according to any one of Claims 1 to 13.

[Claim 15] The tire according to Claim 14, wherein the tire comprises a tread comprising a laminate according to any one of Claims 1 to 13.

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2019/029947

A. CLASSIFICATION OF SUBJECT MATTER
INV. B32B7/027 B32B25/04 B32B25/02 B32B25/14 B32B25/16
B60C1/00
ADD.
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)
B32B

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2018/221630 A1 (MICHELIN & CIE [FR]) 6 December 2018 (2018-12-06) paragraph [0017] - paragraph [0020] paragraph [0033] - paragraph [0035] paragraph [0042] - paragraph [0046] paragraph [0068] - paragraph [0076] paragraph [0109] paragraph [0123] - paragraph [0124] paragraph [0147] paragraph [0169] paragraph [0185] - paragraph [0187] paragraph [0203] figure 4 tables 1-3	1-15

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent but published on or after the international filing date

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"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

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"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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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 March 2020	12/03/2020

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2019/029947

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2004/050469 A1 (SANDSTROM PAUL HARRY [US]) 18 March 2004 (2004-03-18) paragraph [0002] - paragraph [0005] paragraph [0035] - paragraph [0040] -----	1-15
A	WO 2018/079801 A1 (CIE GEN ETAB MICHELIN & CIE) 3 May 2018 (2018-05-03) paragraph [0016] paragraph [0052] - paragraph [0059] paragraph [0078] - paragraph [0081] paragraph [0090] - paragraph [0092] -----	1-15

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/JP2019/029947

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