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(71) Applicant: **Toray Industries, Inc.**
Tokyo 103-8666 (JP)

(72) Inventors:
- **MANABE, Takao**
  Okazaki-shi, Aichi 444-8522 (JP)
- **NISHIHATA, Shinichi**
  Okazaki-shi, Aichi 444-8522 (JP)
- **KATO, Yasutaka**
  Okazaki-shi, Aichi 444-8522 (JP)

(74) Representative: **Mewburn Ellis LLP**
Aurora Building
Counterslip
Bristol BS1 6BX (GB)

(54) RUBBER/FIBER ADHESION TREATING AGENT AND SYNTHETIC FIBER CORD FOR RUBBER REINFORCEMENT USING SAME

(57) An object of the present invention is to provide an adhesive treatment agent for rubber and fiber and a synthetic fiber cord for rubber reinforcement, which are composed of an adhesive treatment agent not containing resorcin or formalin and using a raw material advantageous for reducing an environmental load, which exhibit an initial adhesive force equal to or more than that of conventional RFLs, which are less likely to cause adhesive deterioration under a high temperature for a long time in a state of being embedded in rubber, and which have suppressed strength deterioration when repeatedly stretched and compressed in rubber. An object of the present invention is also to provide an adhesive treatment agent for rubber and fiber and a synthetic fiber cord for rubber reinforcement which have a good storage stability of an adhesive treatment agent, can suppress generation of a resin solidified product in a dipping process, and have a good productivity. The gist of the present invention is an adhesive treatment agent for rubber and fiber, the adhesive treatment agent containing at least: a lignin derivative (A); a water-soluble or water-dispersible crosslinking agent (B); and a rubber latex (C), the adhesive treatment agent not containing a resorcin-formaldehyde resin, wherein the lignin derivative (A) has a number average molecular weight of 10,000 to 60,000 and a weight average molecular weight of 80,000 to 130,000.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a novel adhesive treatment agent which is advantageous for reducing an environmental load and a synthetic fiber cord for rubber reinforcement.

BACKGROUND ART

[0002] Synthetic fibers such as nylon fibers, polyester fibers, and aromatic polyamide fibers are widely used as reinforcing materials for rubber products such as tires, hoses, and belts. As a means for bonding these synthetic fibers and a rubber composition in the rubber product, an RFL (resorcin-formalin-latex) adhesive containing resorcin, formalin, and a rubber latex has been widely used heretofore. However, both resorcin and formalin are deleterious substances, have a high environmental load, and in recent years, it has been required to suppress release of these substances into the atmosphere at the time of use, and to reduce the amount of use due to health hazard.

[0003] Meanwhile, adhesive treatment agents for rubber and fiber represented by the RFL adhesive have problems in storage stability after preparation, such as a change in viscosity over time or the like of the adhesive treatment agent liquid, and a change in the resin adhesion amount or a change in adhesive force or physical properties associated with these changes.

[0004] In addition, it is essential to treat the fiber surface with an adhesive represented by the RFL in order to cause the fiber to have adhesiveness to the rubber. However, in the adhesive treatment process, there is a problem that solidified product caused by the adhesive to be applied adhere to a treatment apparatus such as rollers of a dipping machine, and deteriorate operability.

[0005] As a technique disclosed for the above problems, for example, there are prior arts of Patent Documents 1 to 6.

[0006] Patent Document 1 discloses an adhesive composition for an organic fiber cord, containing a urethane resin having a thermally dissociable blocked isocyanate group, an epoxy compound, a polymer having an oxazoline group, a basic catalyst having a number average molecular weight of 1,000 to 75,000, and a rubber latex.

[0007] Patent Document 2 discloses a processing method in which a woven fabric reinforcing member is immersed in a bath containing a polycarboxylic acid, a base, an epoxy compound, a polyisocyanate compound, and a VP latex.

[0008] Patent Document 3 discloses an aqueous adhesive composition containing a thermosetting resin having a specific functional group and an unsaturated elastomer latex.

[0009] Patent Document 4 discloses an adhesive for an organic fiber, containing at least one component selected from the group consisting of polyphenols, chlorophenol resins and lignin resins, and at least one component selected from water-soluble polymers other than the above components or water-dispersible polymers other than the above components.

[0010] Patent Document 5 discloses an aqueous adhesive composition containing a tri- or more functional specific blocked isocyanate oligomer, a latex, a polyacrylate or a lignin compound, and an additive.

[0011] Patent Document 6 discloses a method for producing an adhesive composition having good storage stability, the method including aging an adhesive composition in a state of containing resorcin and formaldehyde and not containing an alkali catalyst, and then adding a rubber latex to form a mixed liquid.

PRIOR ART DOCUMENT

PATENT DOCUMENTS

[0012]

Patent Document 1: Japanese Patent Laid-open Publication No. 2013-64037
Patent Document 2: Japanese Translation of PCT International Application Publication No. 2020-525622
Patent Document 3: Japanese Translation of PCT International Application Publication No. 2019-518087
Patent Document 4: WO 2018/003572
Patent Document 5: US 2020/0024416 A
Patent Document 6: Japanese Patent Laid-open Publication No. 2013-10909

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0013] However, according to Patent Documents 1 and 5, the initial adhesive force and the heat-resistant adhesive force are developed to be similar to conventional RFLs, but the fatigue resistance in rubber is not sufficient. According to Patent Documents 2, 3, and 4, the initial adhesive force is developed to be similar to conventional RFLs, but the heat-resistant adhesive force and the fatigue resistance in rubber are not sufficient. In addition, in Patent Documents 1 and 2, a compound derived from fossil fuel is used as a substitute for resorcin and formalin, which is slightly disadvantageous for reducing an environmental load. According to Patent Document 6, the storage stability of the adhesive treatment agent is improved, but a conventional RFL adhesive is used, and there is a problem that the environmental load is large. In addition, in all of Patent Documents 1 to 6, a problem that a resin solidified product is generated in a dipping process remains. That is, in order to obtain practical durability in rubber products such as tires, hoses, and belts, an adhesive treatment agent that satisfies all of performances required as a synthetic fiber cord for rubber reinforcement, such as initial adhesive force, heat-resistant adhesive force, and fatigue resistance, also has good storage stability, and is advantageous for reducing an environmental load has not been obtained.

[0014] The present invention has been made as a result of studying the solution of the above-mentioned problems in the prior art as an object.

[0015] An object of the present invention is to provide a novel adhesive treatment agent that does not contain resorcin or formalin and uses a raw material advantageous for reducing an environmental load, and a synthetic fiber cord for rubber reinforcement that uses the adhesive treatment agent, exhibits an initial adhesive force equal to or more than that of conventional RFLs, is less likely to cause adhesive deterioration under a high temperature for a long time in a state of being embedded in rubber, and has suppressed strength deterioration when repeatedly stretched and compressed in rubber. Furthermore, the present invention provides an adhesive treatment agent for rubber and fiber and a synthetic fiber cord for rubber reinforcement that have good storage stability of the adhesive treatment agent, can suppress generation of a resin solidified product in a dipping process, and have good productivity.

SOLUTIONS TO THE PROBLEMS

[0016] In order to solve the above-described problems, the present invention includes the following means.

[0017] That is,

(1) An adhesive treatment agent for rubber and fiber, the adhesive treatment agent containing at least: a lignin derivative (A); a water-soluble or water-dispersible crosslinking agent (B); and a rubber latex (C), the adhesive treatment agent not containing a resorcin-formaldehyde resin, in which the lignin derivative (A) has a number average molecular weight of 10,000 to 60,000 and a weight average molecular weight of 80,000 to 130,000.

(2) The adhesive treatment agent for rubber and fiber according to (1), in which a content of the lignin derivative (A) is 5 to 50 wt% when a total solid content contained in the adhesive treatment agent is 100 wt%, a solid content weight ratio of the lignin derivative (A) to the water-soluble or water-dispersible crosslinking agent (B) is (solid content of A) : (solid content of B) = 10 : 1 to 10 : 20, and when the adhesive treatment agent is formed into a dry film, the dry film has a maximum point strength of 0.2 MPa to 1.6 MPa, and a maximum point elongation of 2% to 1200.

(3) The adhesive treatment agent for rubber and fiber according to (1) or (2), in which the water-soluble or water-dispersible crosslinking agent (B) contains at least one compound selected from the group consisting of an oxazoline group-containing compound, an epoxy compound, and a blocked isocyanate compound.

(4) The adhesive treatment agent for rubber and fiber according to any one of (1) to (3), in which the water-soluble or water-dispersible crosslinking agent (B) is an HDI-based blocked isocyanate or an MDI-based oxime blocked isocyanate.

(5) The adhesive treatment agent for rubber and fiber according to any one of (1) to (4), in which in the adhesive treatment agent, a solid content weight ratio of the lignin derivative (A) and the water-soluble or water-dispersible crosslinking agent (B) to the rubber latex (C) is ((solid content of A) + (solid content of B)) : (solid content of C) = 10 : 90 to 60 : 40.

(6) The adhesive treatment agent for rubber and fiber according to any one of (1) to (5), in which a change rate V_{30}/V_0 of a liquid viscosity (V_{30} (mPa·s)) of the adhesive treatment agent after 30 days with respect to a liquid viscosity (V_0 (mPa·s)) of the adhesive treatment agent after liquid preparation is 90 to 1200.

(7) A synthetic fiber cord for rubber reinforcement, the synthetic fiber cord being obtained by adhering the adhesive treatment agent for rubber and fiber according to any one of (1) to (6) to a synthetic fiber and performing a heat treatment.

EFFECTS OF THE INVENTION

[0018] According to the present invention, a novel adhesive treatment agent and a synthetic fiber cord for rubber reinforcement, which do not contain resorcin or formalin and use a raw material advantageous for reducing the environmental load, are obtained, and such materials exhibit initial adhesive force equal to or more than that of conventional RFLs, are less likely to cause adhesive deterioration under a high temperature for a long time in a state of being embedded in rubber, have suppressed strength deterioration when repeatedly stretched and compressed in rubber, and can be suitably used for rubber reinforcement. In addition, it is possible to provide an adhesive treatment agent for rubber and fiber and a synthetic fiber cord for rubber reinforcement which have good storage stability of the adhesive treatment agent, can suppress generation of a resin solidified product in a dipping process, and have good productivity.

EMBODIMENTS OF THE INVENTION

[0019] Hereinafter, the present invention will be described in detail.

[0020] The adhesive treatment agent for rubber and fiber according to the present invention is capable of exhibiting adhesiveness to rubber when a synthetic fiber is treated, and it is necessary that adhesive treatment agent for rubber and fiber contains at least a lignin derivative (A), a water-soluble or water-dispersible crosslinking agent (B), and a rubber latex (C), and does not contain a resorcin-formaldehyde resin.

[0021] The lignin derivative (A) used in the present invention is a lignin derivative obtained by chemically treating lignin present in a tree which is biomass. Examples of the lignin include kraft lignin obtained from kraft pulp waste liquid, lignin sulfonic acid or lignin sulfonate obtained from sulfite pulp waste liquid, and the like in the papermaking industrial process using wood as a raw material. Lignin sulfonic acid is obtained by introducing a sulfone group into a side chain of the phenylpropane structure of lignin. Examples of the lignin sulfonate include sodium lignin sulfonate, magnesium lignin sulfonate, and calcium lignin sulfonate. In the present invention, these can be used alone or in combination, and among them, sodium lignin sulfonate can be most preferably used from the viewpoint of adhesive force.

[0022] The lignin derivative (A) used in the present invention is required to have a number average molecular weight of 10,000 to 60,000 and a weight average molecular weight of 80,000 to 130,000, and preferably has a number average molecular weight of 20,000 to 50,000 and a weight average molecular weight of 90,000 to 120,000. When the number average molecular weight and the weight average molecular weight exceed the upper limit of this range, the fatigue resistance may be insufficient, the storage stability of the adhesive treatment agent may be deteriorated, or many solidified products may be generated in the dipping process, thus making continuous production difficult. When the number average molecular weight and the weight average molecular weight are less than the lower limit of this range, the initial adhesive force with rubber and the fatigue resistance are deteriorated, which is not preferable. In addition, the ratio of the weight average molecular weight (Mw) to the number average molecular weight (Mn) is preferably 2.5 to 5.0, and more preferably 2.8 to 4.7. When the ratio is out of this range, the adhesive force and fatigue resistance may be insufficient. The number average molecular weight and the weight average molecular weight in the present invention refer to values measured by the methods described in the section of Examples.

[0023] The water-soluble or water-dispersible crosslinking agent (B) used in the present invention is a compound having a functional group capable of reacting with another compound by heating, and is a water-soluble or emulsion-type water-dispersible compound. Specifically, the water-soluble or water-dispersible crosslinking agent (B) preferably contains at least one compound selected from the group consisting of an oxazoline group-containing compound, an epoxy compound, and a blocked isocyanate compound.

[0024] The oxazoline group-containing compound refers to a compound containing an oxazoline group (preferably, a 2-oxazoline group) at a terminal or a side chain of a general organic compound or a substance having an organic polymer and/or oligomer as a main skeleton. The oxazoline group-containing compound may have one or two or more oxazoline groups in one molecule, and more preferably has a large number of oxazoline groups as reactive functional groups in order to improve adhesion performance. As the skeleton of the main chain of the oxazoline group-containing compound, hydrocarbon chains, ethylene glycol chains, and initial polymers of a bisphenol such as bisphenol A, a phenol resin, a novolak resin, a resol resin, and the like are used, and substances containing an aromatic ring or a heterocyclic ring in the molecular skeleton thereof are also used. Furthermore, substances containing an oxazoline group at a terminal or side chain of a main constituent monomer and/or a polymer or oligomer composed thereof are also useful. As these monomers, styrene, styrene derivatives, acrylonitrile, methacrylic acid esters, methacrylic acid, ethylene, butadiene, acrylamide, and the like are used, and these monomers are used as a single polymer and/or oligomer, and further as a copolymer substance. These monomers can also be used as a mixture thereof.

[0025] The oxazoline group-containing compound can be used in a liquid form, a molten form, a solid form, a solution form in which the compound is dissolved in water or an organic solvent that can dissolves the compound, or a suspension form (emulsion particles, latex particles, etc.) in which the compound is dispersed in water or the like. For example, a method of emulsifying or dissolving such a compound as it is or a solution prepared by dissolving such a compound in

a small amount of solvent as necessary, using a known emulsifier such as sodium alkylbenzene sulfonate, dioctyl sulfosuccinate sodium salt, or nonylphenol ethylene oxide adduct may be employed.

[0026] The epoxy compound has two or more epoxy groups in one molecule. Examples of the compound having two or more epoxy groups in the molecule include a glycidyl ether type epoxy resin obtained from a compound having a hydroxyl group in the molecule, a glycidyl amine type epoxy resin obtained from a compound having an amino group in the molecule, a glycidyl ester type epoxy resin obtained from a compound having a carboxyl group in the molecule, a cyclic aliphatic epoxy resin obtained from a compound having an unsaturated bond in the molecule, a heterocyclic epoxy resin such as triglycidyl isocyanurate, and an epoxy resin in which two or more types selected from these are mixed in the molecule.

[0027] Specific examples of the glycidyl ether type epoxy resin that can be used include a bisphenol A type epoxy resin obtained by a reaction between bisphenol A and a halogen-containing epoxide such as epichlorohydrin, a bisphenol F type epoxy resin obtained by a reaction between bisphenol F and the halogen-containing epoxide, a biphenyl type epoxy resin obtained by a reaction between biphenyl and the halogen-containing epoxide, a resorcinol type epoxy resin obtained by a reaction between resorcinol and the halogen-containing epoxide, a bisphenol S type epoxy resin obtained by a reaction between bisphenol S and the halogen-containing epoxide, a polyethylene glycol type epoxy resin which is a reaction product between a polyhydric alcohol and the halogen-containing epoxide, a polypropylene glycol type epoxy resin, an epoxy resin obtained by oxidizing an unsaturated bond moiety of bis-(3,4-epoxy-6-methyl-dicyclohexylmethyl)adipate and 3,4-epoxycyclohexene epoxide or the like, a naphthalene type epoxy resin, a phenol novolak type epoxy resin, a cresol novolak type epoxy resin, and a halogen or alkyl-substituted derivative thereof.

[0028] The blocked isocyanate compound used in the present invention releases a blocking agent by heating to produce an active isocyanate compound. Examples of the blocked isocyanate compound include reaction products of a polyisocyanate compound having a skeleton such as tolylene diisocyanate (TDI), meta-phenylenediisocyanate (MDI), diphenylmethane diisocyanate (HDI), hexamethyline diisocyanate, and triphenylmethane triisocyanate with a blocking agent, for example, phenols such as phenol, cresol, and resorcin, lactams such as ε-caprolactam and valerolactam, and oximes such as acetoxime, methylethylketoxime, and cyclohexanoxime.

[0029] Among these blocked isocyanate compounds, in particular, from the viewpoint of obtaining good adhesive force and fatigue resistance, it is most preferable to select from an HDI-based blocked isocyanate which is a reaction product of hexamethylene diisocyanate and a blocking agent, or an MDI-based oxime blocked isocyanate which is a reaction product of diphenylmethane diisocyanate and a blocking agent of oximes. The diphenylmethane diisocyanate (MDI) can be selected from 2,2'-MDI, 2,4'-MDI, and 4,4'-MDI, and monomeric MDI of 4-4'-MDI is most preferable from the viewpoint of adhesive force and fatigue resistance. Polymeric MDI in which the isocyanate group has a trifunctional group is not preferable because adhesive force and fatigue resistance may be deteriorated. The dissociation temperature of the blocking agent of the HDI-based blocked isocyanate or the MDI-based oxime blocked isocyanate is preferably 100 to 160°C. When the dissociation temperature is in this range, reactivity at the time of heat treatment is good, and higher adhesive force can be exhibited, which is preferable.

[0030] Examples of the rubber latex (C) that can be used in the present invention include natural rubber latex, butadiene rubber latex, styrene-butadiene-rubber latex, vinylpyridine-styrene-butadiene rubber latex, nitrile rubber latex, hydrogenated nitrile rubber latex, chloroprene rubber latex, chlorosulfonated rubber latex, and ethylene-propylene-diene rubber latex, and these latexes can be used alone or in combination.

[0031] The present invention does not contain a resorcin-formaldehyde resin. Here, the resorcin-formaldehyde resin is a compound obtained by reacting resorcin with formaldehyde. For example, a resorcin-formaldehyde resin is obtained by mixing resorcin and formaldehyde in an alkaline aqueous solution containing an alkaline compound such as sodium hydroxide, and allowing the mixture to stand at room temperature for several hours to thereby proceed a condensation reaction between resorcin and formaldehyde.

[0032] In addition to the components (A), (B), and (C), a surfactant, an antifoaming agent, a vulcanization modifier, an antioxidant, and a pH adjuster may be added as necessary to the adhesive treatment agent that can be used in the present invention within a range not hindering the object and effect of the present invention.

[0033] In the adhesive treatment agent of the present invention, when the total solid content contained in the adhesive treatment agent is 100 wt%, the content of the lignin derivative (A) is preferably 5 to 50 wt%, more preferably 7 to 45 wt%, and still more preferably 10 to 40 wt%. When the content is less than 5 wt% or more than 50 wt%, adhesive force and fatigue resistance may be insufficient. Here, the total solid content refers to components excluding the solvent of the adhesive treatment agent.

[0034] The solid content weight ratio of the lignin derivative (A) to the water-soluble or water-dispersible crosslinking agent (B) is preferably (solid content of A) : (solid content of B) = 10 : 1 to 10 : 20, and more preferably 10 : 5 to 10 : 20. When the amount of the crosslinking agent (B) is small in a range exceeding this weight ratio, the adhesive force may be insufficient. When the amount of the crosslinking agent (B) is large in a range exceeding this weight ratio, the cord may be hardened, and the fatigue resistance in rubber may be deteriorated, and when a synthetic fiber cord is used for reinforcing a rubber product such as a tire, a belt, or a hose, the durability of the product may be deteriorated, which is

not preferable.

[0035] In addition, the solid content weight ratio of the lignin derivative (A) and the water-soluble or water-dispersible crosslinking agent (B) to the rubber latex (C) is preferably ((solid content of A) + (solid content of B)) : (solid content of C) = 10 : 90 to 60 : 40, and more preferably 20 : 80 to 50 : 50. When the solid content weight ratio is out of this range, the adhesive force may be insufficient or the fatigue resistance may be deteriorated.

[0036] In the adhesive treatment agent of the present invention, when the adhesive treatment agent is formed into a dry film, the maximum point strength of the dry film is preferably 0.2 MPa to 1.6 MPa, more preferably 0.3 MPa to 1.4 MPa, and still more preferably 0.5 MPa to 1.4 MPa. When the maximum point strength is less than 0.2 MPa, the adhesive force may be insufficient, and when the maximum point strength exceeds 1.6 MPa, the fatigue resistance may be deteriorated. The maximum point elongation of the dry film is preferably 2% to 1200, more preferably 4% to 100%, and still more preferably 20% to 100%. When the maximum point elongation is less than 20, the fatigue resistance may be deteriorated, and when the maximum point elongation is more than 1200, the adhesiveness may be insufficient. The method for adjusting the dry film and the method for measuring the maximum point strength and the maximum point elongation are as described in the section of Examples. However, when it is difficult to use this method, a method equivalent thereto can be used.

[0037] The maximum point strength and the maximum point elongation of the dry film of the adhesive treatment agent can be adjusted by the type of the chemical contained in the adhesive treatment agent and the mixing ratio. The maximum point strength can be adjusted to be high by, for example, increasing the content of the water-soluble or water-dispersible crosslinking agent (B) contained in the adhesive treatment agent. The maximum point elongation can also be adjusted to be high by increasing the mixing amount of the rubber latex (C).

[0038] In the adhesive treatment agent of the present invention, the liquid viscosity (V_0 (mPa·s)) after liquid preparation is preferably 1.0 to 3.0 mPa·s, and more preferably 1.1 to 2.7 mPa·s. When the liquid viscosity is less than 1.0, the amount of the adhesive treatment agent adhered to the synthetic fiber may be insufficient, so that the adhesive force may be deteriorated. When the liquid viscosity is more than 3.0, the amount of the adhesive treatment agent adhered to the synthetic fiber may be conversely excessive, so that continuous production may be difficult due to reduction in adhesive force and generation of solidified products in the dipping process.

[0039] Furthermore, in the present invention, the change rate V_{30}/V_0 of the liquid viscosity (V_{30} (mPa·s)) after 30 days with respect to the liquid viscosity (V_0 (mPa·s)) after liquid preparation is preferably 90 to 1200, more preferably 92 to 110%, and still more preferably 95 to 110%. Although a specific method for measuring the viscosity will be described later, the viscosity change rate in the same test is utilized in the present invention as a measure for achieving the storage stability of the adhesive treatment agent. When the viscosity change rate is less than 90% or more than 1200, the amount of the adhesive treatment agent adhering to the synthetic fiber in the dipping process changes along with the viscosity change of the adhesive treatment agent. As a result, the adhesive force may decrease, or solidified products may be generated in the dipping process and continuous production may be difficult.

[0040] As the method for setting the liquid viscosity of the adhesive treatment agent within the specified range of the present invention, the liquid viscosity can be adjusted by, for example, optimizing the selection of the type and blending ratio of the lignin derivative (A), the water-soluble or water-dispersible crosslinking agent (B), and the rubber latex (C) to be used. In addition, a surfactant may be added as appropriate. Examples of the surfactant include alkyl sulfuric acid ester salts, polyoxyethylene alkyl ether sulfuric acid ester salts, and alkyl benzenesulfonic acid salts.

[0041] The adhesive treatment agent of the present invention is an agent in which a solid content is dissolved or dispersed in water. The total solid content concentration is preferably 5 to 25 wt%, more preferably 10 to 20 wt%, and still more preferably 12 to 18 wt%. When the total solid content concentration is out of this range, the adhesive force may be reduced. When the total solid content concentration is out of this range, a sufficient amount of solid content may not be imparted to the fiber, or cohesive failure in the adhesive solid content may occur, which may lead to a decrease in adhesive force.

[0042] The synthetic fiber cord for rubber reinforcement of the present invention can be suitably used for reinforcing rubber, and is obtained by treating a synthetic fiber with the above-described adhesive treatment agent for rubber and fiber.

[0043] The term "treated" means a state in which the adhesive treatment agent is applied to the synthetic fiber and then a drying treatment or a heat treatment is performed. In the drying treatment and the heat treatment, for example, a volatile component contained in the adhesive treatment agent, for example, a solvent such as water is distilled off. For example, when a blocked isocyanate compound is used for the crosslinking agent (B), the blocking agent is removed, and a reaction due to an isocyanate group occurs. That is, in the synthetic fiber treated with the adhesive treatment agent, the solid content in a state of being chemically modified or not modified in the adhesive treatment agent is adhered to or bonded to the synthetic fiber. The adhesive treatment agent of the present invention refers to an adhesive treatment agent containing at least a lignin derivative (A), a water-soluble or water-dispersible crosslinking agent (B), and a rubber latex (C) in the same bath (one bath), and does not contain the components (A), (B), and (C) separately in each of the first bath adhesive and the second bath adhesive in, for example, a so-called two bath treatment method known as a method for treating polyester fibers. Furthermore, it is necessary that neither the first bath adhesive nor the second bath

adhesive contain a resorcin-formaldehyde resin.

[0044] Here, regarding the amount of the adhesive treatment agent adhered to the synthetic fiber, the solid content weight of the adhesive treatment agent based on 100 parts by weight of the synthetic fiber is preferably 1 part by weight to 15 parts by weight, and more preferably 1.5 parts by weight to 10 parts by weight. When the solid content weight is out of this range, the adhesive force may be reduced.

[0045] The synthetic fiber that can be used in the present invention is preferably in the form of multifilaments. Examples of the material constituting the synthetic fiber include nylon fibers, polyester fibers, aramid fibers, and polyvinyl alcohol fibers. Particularly, the synthetic fiber preferably contains at least one selected from polyester fibers, nylon fibers, and aramid fibers from the viewpoint of durability and industrial productivity. At least one fiber selected from polyester fibers, nylon fibers, and aramid fibers preferably accounts for 60 wt% or more, preferably 80 wt% or more, and more preferably 90 wt% or more based on 100 wt% of the total weight of the synthetic fiber.

[0046] Examples of the polyester fiber include fibers made of polyethylene terephthalate and polyethylene naphthalate. The polyester fiber is desirably a fiber obtained by melt-spinning and drawing a polyester containing terephthalic acid as a main bifunctional carboxylic acid and ethylene glycol as a main glycol component. The polyester fiber to be used may be a fiber made of a polyester in which terephthalic acid is partially or entirely replaced with 2,6-naphthalenedicarboxylic acid, 4,4-dicarboxyphenoxyethane, an isocyanate group, or the like, or a polyester in which ethylene glycol is partially or entirely replaced with diethylene glycol, propylene glycol, butanediol, or the like.

[0047] The polyester may be a copolymer of a trifunctional compound such as trimesic acid, trimellitic acid, boric acid, phosphoric acid, glycerin, or trimethylolpropane if the amount is small.

[0048] The polyester fiber may be modified with various modifiers, for example, a terminal carboxyl group capping agent such as a carbodiimide compound, an epoxy compound, an isocyanate compound, and an oxazoline compound.

[0049] The polyester fiber may also be a polyester fiber to which a polyepoxide compound has been applied in advance in the spinning process. Examples of the polyepoxide compound include compounds containing at least 2 or more epoxy groups in one molecule in an amount of 0.1 g equivalent or more per 100 g of the compound. Specific examples of the polyepoxide compound include reaction products of a polyhydric alcohol such as pentaerythritol, ethylene glycol, polyethylene glycol, propylene glycol, glycerol, or sorbitol and a halogen-containing epoxide such as epichlorohydrin; polyepoxide compounds obtained by oxidizing an unsaturated compound with peroxide, hydrogen peroxide, or the like; compounds such as 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexenecarboxylate, and bis(3,4-epoxy-6-methyl-cyclohexylmethyl)adipate; and aromatic polyepoxides such as phenol novolak type, hydroquinone type, biphenyl type, bisphenol S type, brominated novolak type, xylene modified novolak type, phenol glyoxal type, trisoxyphenylmethane type, trisphenol PA type, and bisphenol type polyepoxides. The polyepoxide compound is particularly preferably a sorbitol glycidyl ether type polyepoxide or a cresol novolak type polyepoxide.

[0050] These polyepoxide compounds are usually used as an emulsion or a solution. That is, the compound is dissolved in a solvent and used as a solution, or emulsified using an ordinary emulsifier, for example, sodium alkylbenzene sulfonate, dioctyl sulfosuccinate sodium salt, nonylphenol ethylene oxide adduct, or the like, and used as an emulsion.

[0051] The polyepoxide compound is applied together with a spinning oil agent in the spinning process of the synthetic fiber. The adhesion amount of the polyepoxide compound at this time is preferably in a range of 0.1 to 5 wt%. When the adhesion amount of the polyepoxide compound is within the above range, the effect of the polyepoxide compound is sufficiently exhibited, and satisfactory adhesiveness between the synthetic fiber and rubber is obtained. When the adhesion amount of the polyepoxide compound is within the above range, the fiber does not become too hard, and the strength is less likely to decrease in the twisting process described later.

[0052] Examples of the nylon fiber include fibers made of nylon 6, nylon 66, nylon 46, nylon 610, nylon 612, and the like. Among them, fibers made of high-molecular-weight nylon 66 having a sulfuric acid relative viscosity of 3.0 or more, more preferably 3.5 or more are preferable. The nylon fiber may contain conventionally known inorganic and organic copper salts or a single copper metal as well as copper compounds. The nylon fiber may contain, in addition to the copper compound, other heat resistant agents such as an amine compound, a mercapto compound, a phosphorus compound, and a hindered phenol compound.

[0053] When the nylon fiber is used as a tire cord, a polymer having a high degree of polymerization is used to obtain a fiber having high strength and high toughness, and a fiber having a sulfuric acid relative viscosity of 3.0 to 5.0 is preferably used as the fiber.

[0054] The aramid fiber is not particularly limited as long as it is a fiber usually having at least one divalent aromatic group optionally substituted and at least one amide bond in repeating units of a polymer forming the fiber, and may be a known fiber referred to as a wholly aromatic polyamide fiber or an aramid fiber. In the above, the "divalent aromatic group optionally substituted" means a divalent aromatic group which optionally has one or more same or different substituents.

[0055] The aramid fiber includes para-aramid fibers and meta-aramid fibers. In the present invention, para-based aramid fibers having excellent tensile strength can be preferably used. Examples of the para-aramid fiber include polyparaphenylene terephthalamide fibers (manufactured by U.S. DuPont, Du Pont-Toray Co., Ltd., product name "Kevlar"

(registered trademark)) and co-poly-(paraphenylene-3,4'-oxydiphenylene terephthalamide) fibers (product name "Technora" (registered trademark) manufactured by Teijin Limited).

[0056] The synthetic fiber used in the present invention is not limited by the fineness, the number of filaments, the cross-sectional shape, and the like, but usually a circular cross-sectional yarn having a total fineness of 200 to 5,000 dtex and 30 to 1,000 filaments is used, and a circular cross-sectional yarn having a total fineness of 250 to 3,000 dtex and 50 to 500 filaments are preferable. When the total fineness is less than 200 dtex, the strength of the cord may be insufficient, and when the total fineness is more than 5,000 dtex, the cord may be thick and the handleability may be deteriorated. When the number of filaments is less than 30, the cord may become hard and the handleability may be deteriorated, and when the number of filaments exceeds 1,000, the fuzz may increase and the quality may be deteriorated.

[0057] From the viewpoint of improving the fatigue resistance, the synthetic fiber cord of the present invention can be obtained by twisting the synthetic fibers to form a twisted cord, subjecting the twisted cord as it is or a cord fabric obtained by weaving the twisted cord to a dip treatment with the adhesive treatment agent of the present invention, and performing a heat treatment. For example, as a twisted cord used for a carcass tire cord, a twisted cord obtained by first-twisting fibers in the S direction or the Z direction, then combining two or three first-twisted cords, and usually, second-twisting the first-twisted cords with the same number of twists as the number of the first twists in a direction reverse to the first twist to form a twisted cord as a plied cord can be used. A gray cord fabric is woven using, as warp, the twisted cord and as weft, a cotton yarn or a yarn obtained by covering an organic fiber with a cotton yarn. Then, the gray cord fabric is subjected to a dip treatment with an adhesive treatment agent and then heat-treated to obtain a dipped fabric.

[0058] On the other hand, in the case of a cord for a hose or belt, for example, a twisted cord is formed by first-twisting fibers, or formed by combining two or three first-twisted cords and usually, second-twisting the first-twisted cords with the same number of twists as the number of first twists in a direction reverse to the first twist to form a twisted cord as a plied cord, and the twisted cord is subjected to a dip treatment with an adhesive treatment agent and then heat-treated to form a dipped cord.

[0059] The synthetic fiber cord treated with the adhesive treatment agent of the present invention includes both the case of the dipped fabric and the case of the dipped cord.

[0060] The synthetic fiber cord for rubber reinforcement of the present invention may be treated with a precoating agent before the synthetic fiber is treated with the adhesive treatment agent (adhesive treatment agent containing at least the components (A), (B) and (C)).

[0061] The precoating agent contains at least an epoxy compound, and the concentration of the total solid content in the precoating agent is preferably 0.1 to 60. More preferably, the precoating agent contains at least an epoxy compound and a blocked isocyanate compound, (the solid content weight of the blocked isocyanate compound)/(the solid content weight of the epoxy compound) is 3 or less, and the concentration of the total solid content in the precoating agent is 0.1 to 60. When the above-described solid content weight ratio and the concentration of the total solid content are out of this range, the adhesive force may be reduced. In addition, regarding the amount of the precoating agent adhered to the synthetic fiber, the solid content weight of the precoating agent based on 100 parts by weight of the synthetic fiber is preferably 0.1 parts by weight to 3 parts by weight. When the solid content weight is out of this range, the adhesive force may be reduced.

[0062] The adhesive treatment agent for rubber and fiber of the present invention characterized by the above is composed of a novel adhesive treatment agent which does not contain resorcin or formalin and uses a raw material advantageous for reducing an environmental load. A synthetic fiber cord for rubber reinforcement using the adhesive treatment agent exhibits an initial adhesive force equal to or more than that of conventional RFLs, is less likely to cause adhesive deterioration under a high temperature for a long time in a state of being embedded in rubber, has suppressed strength deterioration when repeatedly stretched and compressed in rubber, and can be suitably used for rubber reinforcement. In addition, it is possible to provide an adhesive treatment agent for rubber and fiber and a synthetic fiber cord for rubber reinforcement which have good storage stability of the adhesive treatment agent, can suppress generation of a resin solidified product in the dipping process, and have good productivity.

[0063] The synthetic fiber cord for rubber reinforcement of the present invention is obtained by adhering the above adhesive treatment agent for rubber and fiber to a synthetic fiber and performing a heat treatment. The synthetic fiber cord for rubber reinforcement of the present invention can be used for reinforcing rubber products such as tires, belts, and hoses, uses an environmentally friendly adhesive not using resorcin or formalin, and can exhibit performance equal to or more than that using a conventional RFL.

[0064] Next, a method for producing the synthetic fiber cord for rubber reinforcement of the present invention will be described.

[0065] Examples of the method for producing a synthetic fiber cord for rubber reinforcement of the present invention include a method including adhering an adhesive treatment agent which contains at least a lignin derivative (A), a water-soluble or water-dispersible crosslinking agent (B) and a rubber latex (C) and does not contain a resorcin-formaldehyde resin to a synthetic fiber in the same bath and performing a heat treatment. The synthetic fiber may be in the form of a twisted cord or a gray cord fabric. A method is preferable in which the twisted cord or the gray cord fabric is dipped in

an adhesive treatment agent in a dip bath, subsequently moisture is dried at a temperature of preferably 100 to 150°C, and subsequently heat treatment is performed at 200 to 255°C. As preferred aspects of the lignin derivative (A), the water-soluble or water-dispersible crosslinking agent (B), and the rubber latex (C), those described above can be used.

[0066] Here, the dipping refers to applying an adhesive treatment agent to a twisted cord or a gray cord fabric by causing the twisted cord or the gray cord fabric to travel in a dipping tank in which rollers are installed and the adhesive treatment agent is filled. The heat treatment refers to heating the twisted cord or the gray cord fabric by causing the twisted cord or the gray cord fabric to travel in an oven in which rollers are installed and a predetermined temperature can be set. A dip treatment machine for performing such dipping and heat treatment is commercially available, for example, from C. A. Litzler Co., Inc. As another method for adhering the adhesive treatment agent to the synthetic fiber, for example, any method such as application by spraying the adhesive treatment agent from a nozzle can be adopted in addition to the dip treatment.

[0067] In order to control the adhesion amount of the solid content of the adhesive treatment agent to the synthetic fiber, means such as squeezing by a pressure roller, scraping off by a scraper, blowing off by air spraying, and suction may be used.

[0068] Furthermore, at the time of the mechanical softening treatment process after the drying and heat treatment, a softening treatment for obtaining an arbitrary cord stiffness can be performed by bringing the synthetic fiber cord into sliding contact with the edge.

[0069] In the method for producing a synthetic fiber cord for rubber reinforcement of the present invention, the adhesive treatment agent (adhesive treatment agent containing at least the component (A), the component (B), and the component (C)) may be adhered to the synthetic fiber, a precoating agent may be adhered prior to a heat treatment, and then the heat treatment may be performed.

[0070] The precoating agent contains at least an epoxy compound, and the concentration of the total solid content in the precoating agent is preferably 0.1 to 60. More preferably, the precoating agent contains at least an epoxy compound and a blocked isocyanate compound, (the solid content weight of the blocked isocyanate compound)/(the solid content weight of the epoxy compound) is 3 or less, and the concentration of the total solid content in the precoating agent is 0.1 to 60. When the above-described solid content weight ratio and the concentration of the total solid content are out of this range, the adhesive force may be reduced. In addition, regarding the amount of the precoating agent adhered to the synthetic fiber, the solid content weight of the precoating agent based on 100 parts by weight of the synthetic fiber is preferably 0.1 parts by weight to 3 parts by weight. When the solid content weight is out of this range, the adhesive force may be reduced.

[0071] In the case of adhering the precoating agent, a dipping method similar to the above method can be adopted. That is, a method is preferable in which a twisted cord or a gray cord fabric of the synthetic fiber is dipped in a precoating agent in a dip bath, subsequently moisture is dried at a temperature of preferably 100 to 150°C, and subsequently heat treatment is performed at 200 to 255°C. The same method as described above can be adopted for the control of the adhesion amount of the solid content and the softening treatment.

[0072] The adhesive treatment agent for rubber and fiber and the synthetic fiber cord for rubber reinforcement of the present invention which are obtained in this way are composed of an advantageous novel adhesive treatment agent which does not contain resorcin or formalin and uses a biomass-derived raw material for reducing an environmental load, exhibit an initial adhesive force equal to or more than that of conventional RFLs, are less likely to cause adhesive deterioration under high temperature for a long time in a state of being embedded in rubber, have suppressed strength deterioration when repeatedly stretched and compressed in rubber, and can be suitably used for rubber reinforcement. In addition, it is possible to provide an adhesive treatment agent for rubber and fiber and a synthetic fiber cord for rubber reinforcement which have good storage stability of the adhesive treatment agent, can suppress generation of a resin solidified product in the dipping process, and have good productivity.

EXAMPLES

[0073] Hereinafter, the present invention will be described more specifically with reference to Examples, but the present invention is not limited by these Examples at all. In Examples and the like described in detail below, each measured value is obtained by the following methods.

(1) Adhesion amount of adhesive treatment agent

[0074] The adhesion amount of the adhesive of the synthetic fiber cord for rubber reinforcement was determined according to the mass method of dip-pickup of JIS L1017 (2002).

(2) Initial adhesive force and heat-resistant adhesive force

[0075] The initial adhesive force and the heat-resistant adhesive force indicate an adhesive force between a synthetic fiber cord and rubber. In the measurement of the initial adhesive force, in accordance with JIS L1017 (2002), Appendix 1, Section 3.1 T test (method A), a synthetic fiber cord for rubber reinforcement was embedded in unvulcanized rubber, this rubber composite was press-vulcanized at 50 kg/cm^2 for 30 minutes at 150°C, and then allowed to cool, the synthetic fiber cord was pulled out from the rubber block at a speed of 300 mm/min, a weight required for the pulling was determined for each sample, and the arithmetic average value of ten samples was taken as the initial adhesive force. In the measurement of the heat-resistant adhesive force, in accordance with JIS L1017 (2002), Appendix 1, Section 3.1 T test (method A), a synthetic fiber cord for rubber reinforcement was embedded in an unvulcanized rubber, this rubber composite was press-vulcanized at 50 kg/cm^2 for 70 minutes at 170°C, and then allowed to cool, the synthetic fiber cord was pulled out from the rubber block at a speed of 300 mm/min, a weight required for the pulling was determined for each sample, and the arithmetic average value of ten samples was taken as the heat-resistant adhesive force.

(3) Fatigue resistance in rubber (retention)

[0076] The fatigue resistance in rubber was evaluated in accordance with JIS L1017 (2002), Appendix 1, Section 2.2.2, Disc Fatigue Strength (Goodrich Method). Two synthetic fiber cords for rubber reinforcement are embedded in unvulcanized rubber, and press-vulcanized under conditions of 150°C, 30 minutes, and 50 kg/cm^2 to prepare a rubber composite. This test piece was subjected to deformation with a compression rate of 6.3% and a stretch rate of 12.6% as 1 cycle at 2,600 cycles/min in an atmosphere of 100°C for 12 hours. Thereafter, the synthetic fiber cord was taken out from the rubber, and the strength at break after fatigue was measured. The retention of the strength at break before and after the fatigue test was determined for each sample, and the arithmetic average value of eight samples was taken as the fatigue resistance in rubber (retention). Here, the strength at break before the fatigue test refers to strength at break, measured by preparing the rubber composite as described above, taking out the synthetic fiber cord from the rubber before performing the fatigue test, and performing a tensile test. That is, the fatigue resistance in rubber (retention) (%) is calculated according to (strength at break of cord taken out from rubber after fatigue test)/(strength at break of cord taken out from rubber before fatigue test) $\times$ 100, and the strength at break of the cord taken out from rubber before the fatigue test is the retention of 100%.

[0077] The composition of the unvulcanized rubber compound used for measurement of the initial adhesive force, the heat-resistant adhesive force, and the fatigue resistance in rubber is as follows.

Natural rubber (RSS #1): 70 (parts by weight)
SBR (#1502, manufactured by JSR Corporation): 30 (parts by weight)
HAF carbon black: 40 (parts by weight)
Stearic acid: 2 (parts by weight)
Sulfur: 2 (parts by weight)
Zinc oxide: 5 (parts by weight)
2,2'-Dithiobenzothiazole: 3 (parts by weight)
Naphthenic acid process oil: 3 (parts by weight).

(4) Measurement of liquid viscosity of adhesive treatment agent

[0078] The liquid viscosity (V_0 (mPa·s)) of the adhesive treatment agent sample after liquid preparation was measured by the method of JIS Z8803 (2011) using a tuning fork vibro viscometer SV-1A manufactured by A&D Company, Limited under an environment of 25°C. Here, the liquid viscosity after liquid preparation refers to a liquid viscosity obtained by performing measurement during a period from immediately after liquid preparation to 1 hour after liquid preparation. The adhesive treatment agent sample was allowed to stand in a thermostatic chamber at 25 $\pm$ 0.5°C, and 30 days after liquid preparation, the liquid viscosity (V_{30} (mPa·s)) was measured by the same method, and the change rate V_{30}/V_0 (%) was calculated.

(5) Generation of solidified product in dipping process

[0079] In the process of performing dipping and heat treatment using Computreater of C. A. Litzler Co., Inc., the twisted cord was immersed in the adhesive treatment agent of the present invention, the cord was allowed to travel at a cord traveling speed of 20 m/min for 1 hour, and then the amount of the solidified product deposited on the turn roll with which the cord was in contact during traveling in an oven at 120°C was visually confirmed. A case where there was no deposit of the solidified product was determined to be S. A case where a small amount of the solidified product was deposited

but there was no practical problem was determined to be A. A case where a large amount of the solidified product was deposited and there was a practical problem was determined to be B. In the present invention, S and A are regarded as acceptable in the processability that can withstand practical use, but S is superior in practical use.

(6) Maximum point strength and maximum point elongation of dry film of adhesive treatment agent

[0080] The adhesive treatment agent was applied to a glass plate so that the thickness of the film after drying was 0.5 mm, and dried at room temperature for 72 hours to obtain a film-like dry film sample in which moisture was dried. The sample was peeled off from the glass plate, heat-treated in an oven at 120°C for 15 minutes, and further heat-treated in an oven at 240°C for 2 minutes. This was punched out in a No. 2 dumbbell shape (width: 1 cm) specified in JIS K6251 (2017) to obtain a sample for tensile test measurement. Using a TENSILON RTM-100 type tester manufactured by Orientec Co., Ltd., the gauge length between upper and lower chucks was set to 50 mm, a sample for measurement was held with the chucks, and a tensile test was performed at a crosshead speed of 50 mm/min in an atmosphere of 25°C to measure the strength and elongation. The strength and elongation at which the strength reached the maximum value were determined for each sample. The arithmetic average value of the strengths of six samples was defined as the maximum point strength, and the arithmetic average value of the elongations of six samples was defined as the maximum point elongation. Here, the maximum point elongation (%) was calculated by the elongation (mm) of the sample at the point where the strength reaches the maximum value ÷ the initial gauge length (50 mm) × 100. For example, when the elongation before the tensile test is 0 mm, the elongation is 0%, and when the elongation after the tensile test is 50 mm, the elongation is 100%.

(7) Measurement of number average molecular weight and weight average molecular weight of lignin derivative

[0081] The number average molecular weight and the weight average molecular weight of the lignin derivative were measured by gel permeation chromatography (GPC). A solvent (ammonia buffer/methanol) was added to the lignin derivative sample, and the lignin derivative sample was dissolved therein by stirring at room temperature, and the resulting solution was filtered through a 0.5 um filter. Thereafter, measurement was performed by GPC, a peak was detected by a UV detector, and the molecular weight was measured by a relative value based on polyethylene oxide and polyethylene glycol. The measurement results are described in Examples described later. Details of the measurement conditions are described below.

Measuring apparatus: manufactured by Shimadzu Corporation
Column used: TSKgel GMPW$_{XL}$ (one column), G3000PW$_{XL}$ (one column) (φ 7.8 mm × 30 cm, manufactured by Tosoh Corporation)
Solvent: 0.1 M ammonia buffer (pH 11)/methanol (4/1, v/v)
Reference material: Monodispersed polyethylene oxide and polyethylene glycol manufactured by Tosoh Corporation and Agilent Technologies, Inc.
Detector: UV detector (SPD-M20A manufactured by Shimadzu Corporation).

(Examples 1 to 10 and Comparative Examples 1 to 6)

[0082] Glycerol polyglycidyl ether ("DENACOL" EX313 (manufactured by Nagase ChemteX Corporation)), a blocked isocyanate compound (DM-6400 (manufactured by Meisei Chemical Works, Ltd.)), and a rubber latex (PYRATEX, manufactured by NIPPON A&L INC.) were mixed so that the solid content ratio was 20 : 40 : 40, and the mixture was diluted with water to obtain a precoating agent (P) having a total solid content of 4.0 wt%.

[0083] In addition, the lignin derivative (A), the water-soluble or water-dispersible crosslinking agent (B), and the rubber latex (C) were mixed with water so that the solid contents of the lignin derivative (A), the water-soluble or water-dispersible crosslinking agent (B), and the rubber latex (C) were the ratios shown in Table 1 or 2 to obtain an adhesive treatment agent having a total solid content concentration of 15 wt%. The maximum point strength and the maximum point elongation of the dry film were measured for the obtained adhesive treatment agents according to the above-described measurement methods. In addition, the change rate V_{30}/V_0 of the liquid viscosity (V_{30} (mPa·s)) after 30 days with respect to the liquid viscosity (V_0 (mPa·s)) after liquid preparation was measured for the adhesive treatment agents according to the above-described measurement method.

[0084] Two polyester multifilament yarns of 1,670 dtex ("TETORON" 1670T-360-705M, manufactured by Toray Industries, Inc.) were twisted with the number of first twists of 40 times/10 cm and the number of second twists of 40 times/10 cm to obtain a twisted cord.

[0085] The twisted cord was immersed in the precoating agent (P) using Computreater (manufactured by C. A. Litzler Co., Inc.), then dried at 120°C for 2 minutes, and subsequently heat-treated at 245°C for 1 minute. Subsequently, the

resultant product was immersed in an adhesive treatment agent containing the components (A), (B) and (C), then dried at 120°C for 2 minutes, and subsequently heat-treated at 240°C for 1 minute to obtain a synthetic fiber cord.

[0086] Here, the treatment with the adhesive treatment agent containing the components (A), (B) and (C) was performed by causing the cord to travel at a traveling speed of 20 m/min for 1 hour. In the Computreater after completion of the treatment, the amount of the solidified product deposited on the turn roll with which the cord was in contact during traveling in the oven at 120°C was confirmed. The generation state of the solidified product was then evaluated according to the method described in Examples.

[0087] Regarding the adhesion amount of the adhesive solid content in the obtained synthetic fiber cord, the solid content weight of the precoating agent was 1.1 parts by weight based on 100 parts by weight of the polyester fiber, and the solid content weight of the adhesive treatment agent containing the components (A), (B), and (C) was 4.0 parts by weight based on 100 parts by weight of the polyester fiber.

[0088] The components of the adhesive treatment agent shown in Tables 1 and 2 are as follows.

(A)-1: Lignin derivative (sodium lignin sulfonate, "VANILLEX" N, manufactured by Nippon Paper Industries Co., Ltd., number average molecular weight: 29,000, weight average molecular weight: 105,000)
(A)-2: Lignin derivative (sodium lignin sulfonate, "VANILLEX" RN, manufactured by Nippon Paper Industries Co., Ltd., number average molecular weight: 34,000, weight average molecular weight: 112,000)
(A)-3: Lignin derivative (sodium lignin sulfonate, "PEARLLEX" NP, manufactured by Nippon Paper Industries Co., Ltd., number average molecular weight: 97,000, weight average molecular weight: 146,000)
(A)-4: Lignin derivative (sodium lignin sulfonate, "SAN X" P252, manufactured by Nippon Paper Industries Co., Ltd., number average molecular weight: 66,000, weight average molecular weight: 135,000)
(B)-1: Blocked isocyanate (oxime blocked diphenylmethane diisocyanate, DM-6400, manufactured by Meisei Chemical Works, Ltd., dissociation temperature: 120 to 160°C)
(B)-2: Blocked isocyanate (blocking agent adduct of hexamethylene diisocyanate, SU-268A, manufactured by Meisei Chemical Works, Ltd., dissociation temperature: 100 to 130°C)
(B)-3: Carbodiimide group-containing polymer (CARBODILITE V-02, manufactured by Nisshinbo Chemical Inc.)
(B)-4: Oxazoline group-containing compound ("EPOCROS" K-2030E, manufactured by Nippon Shokubai Co., Ltd.
(B)-5: Epoxy compound ("DENACOL" EX313, manufactured by Nagase ChemteX Corporation)
(B)-6: Blocked isocyanate (lactam blocked diphenylmethane diisocyanate, DM-3031CONC, manufactured by Meisei Chemical Works, Ltd., dissociation temperature: 160 to 180°C)
(B)-7: Blocked isocyanate (lactam-blocked polymeric MDI, DM-7000, manufactured by Meisei Chemical Works, Ltd., dissociation temperature: 160 to 180°C)
(C)-1: Rubber latex ("PYRATEX", manufactured by NIPPON A&L INC.).

(Conventional Example)

[0089] Treatment and evaluation were performed in the same procedure as in Example 1, except that, in Example 1, the adhesive treatment agent containing the components (A), (B) and (C) was changed to an RFL adhesive obtained in the following procedure. Resorcin and formalin were mixed at a molar ratio of 1/1.5 in the presence of caustic soda, the mixture was adjusted so that the solid content concentration was 10%, and the mixture was aged for 2 hours to obtain an initial condensate of resorcin and formalin. Next, the initial condensate (RF) and a rubber latex (PYRATEX, manufactured by NIPPON A&L INC.) were mixed at a ratio of RF/L = 1/5 (solid content weight ratio), and the mixture was aged for 24 hours. The mixture was diluted with water to obtain an RFL adhesive with a solid content weight of 150. Regarding the adhesion amount of the adhesive solid content in the obtained synthetic fiber cord for rubber reinforcement, the solid content weight of the precoating agent was 1.1 parts by weight based on 100 parts by weight of the polyester fiber, and the solid content weight of the RFL adhesive was 4.0 parts by weight based on 100 parts by weight of the polyester fiber.

[0090] The synthetic fiber cord for rubber reinforcement obtained as described above was embedded in an unvulcanized rubber and vulcanized. Then, the initial adhesive force, the heat-resistant adhesive force, and the fatigue resistance in rubber were measured. The results are shown in Table 2.

[0091] As can be seen from the results in Table 1, in the case of the Examples according to the present invention, the adhesive treatment agent does not contain resorcin or formalin, is advantageous in reducing an environmental load as compared with the RFL of Conventional Example, and has favorable adhesiveness to rubber and heat-resistant adhesiveness, and favorable fatigue resistance under a high-temperature atmosphere. In addition, it is found that the storage stability of the adhesive treatment agent is good, and the generation of a resin solidified product can be suppressed in the dipping process, so that the productivity of the synthetic fiber cord for rubber reinforcement is good.

[Table 1-1]

		Example 1	Example 2	Example 3	Example 4	Example 5
Fiber		Polyester	Polyester	Polyester	Polyester	Polyester
Precoating agent		(P)	(P)	(P)	(P)	(P)
Composition	(A)	**(A) -1**	**(A) -2**	**(A) -1**	**(A) -2**	**(A) -1**
	(B)	**(B) -1**	**(B) -1**	**(B) -2** (B) -2	**(B) -1**	**(B) -1**
	(C)	**(C) -1**	**(C) -1**	**(C) -1**	**(C) -1**	**(C) -1**
Solid content weight ratio	(A)	**20**	**15**	**25**	**4**	**10**
	(B)	**20**	**25**	**15**	**8**	**25**
	(C)	**60**	**60**	**60**	**88**	**65**
Maximum point strength of dry film	MPa	**0.5**	**0.5**	**0.4**	**0.2**	**1.0**
Maximum point elongation of dry film	%	**30**	**30**	**40**	**170**	**20**
Adhesion amount of precoating agent	Parts by weight	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**
Adhesion amount of adhesive treatment agent	Parts by weight	**4.0**	**4.0**	**4.0**	**4.0**	**4.0**
Initial adhesive force	N/cm	**190**	**191**	**187**	**178**	**180**
Heat-resistant adhesive force	N/cm	**175**	**176**	**174**	**160**	**165**
Fatigue resistance in rubber	%	**82**	**81**	**80**	**74**	**71**
Viscosity change rate	V_{30}/V_0	**100**	**100**	**102**	**99**	**100**
Generation of aggregate in dipping process	-	S	S	S	A	A

[Table 1-2]

		Example 6	Example 7	Example 8	Example 9	Example 10
Fiber		Polyester	Polyester	Polyester	Polyester	Polyester
Precoating agent		(P)	(P)	(P)	(P)	(P)
Composition	(A)	**(A) -2**	**(A) -1**	**(A) -2**	**(A) -1**	**(A) -2**
	(B)	**(B) -3**	**(B) -4**	**(B) -5**	**(B) -6**	**(B) -1**
	(C)	**(C) -1**	**(C) -1**	**(C) -1**	**(C) -1**	**(C) -1**
Solid content weight ratio	(A)	**20**	**25**	**15**	**20**	**35**
	(B)	**20**	**25**	**15**	**20**	**35**
	(C)	**60**	**50**	**70**	**60**	**30**
Maximum point strength of dry film	MPa	**0.6**	**0.5**	**0.4**	**0.5**	**1.2**
Maximum point elongation of dry film	%	**20**	**25**	**35**	**30**	**15**

(continued)

		Example 6	Example 7	Example 8	Example 9	Example 10
Fiber		Polyester	Polyester	Polyester	Polyester	Polyester
Precoating agent		(P)	(P)	(P)	(P)	(P)
Adhesion amount of precoating agent	Parts by weight	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**
Adhesion amount of adhesive treatment agent	Parts by weight	**4.0**	**4.0**	**4.0**	**4.0**	**4.0**
Initial adhesive force	N/cm	**180**	**180**	**180**	**186**	**180**
Heat-resistant adhesive force	N/cm	**165**	**166**	**167**	**172**	**172**
Fatigue resistance in rubber	%	**75**	**77**	**78**	**78**	**80**
Viscosity change rate	V_{30}/V_0	**125**	**110**	**99**	**100**	**109**
Generation of aggregate in dipping process	-	A	A	A	S	S

[Table 2]

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Conventional Example
Fiber		Polyester	Polyester	Polyester	Polyester	Polyester	Polyester	Polyester
Precoating agent		(P)	(P)	(P)	(P)	(P)	(P)	(P)
Composition	(A)	**None**	**(A) -1**	**(A) -2**	**(A) -3**	**(A) -3**	**(A) -4**	-
	(B)	**(B) -1**	**None**	**(B) -1**	**(B) -1**	**(B) -7**	**(B) -1**	-
	(C)	**(C) -1**	**(C) -1**	**None**	**(C) -1**	**(C) -1**	**(C) -1**	-
Solid content weight ratio	(A)	**0**	**40**	**50**	**15**	**11**	**15**	-
	(B)	**40**	**0**	**50**	**25**	**28**	**25**	-
	(C)	**60**	**60**	**0**	**65**	**61**	**65**	-
Maximum point strength of dry film	MPa	**0.1**	**0.1**	**2.0**	**0.5**	**0.2**	**0.5**	-
Maximum point elongation of dry film	%	**160**	**140**	**10**	**30**	**15**	**30**	-
Adhesion amount of precoating agent	Parts by weight	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**
Adhesion amount of adhesive treatment agent	Parts by weight	**4.0**	**4.0**	**4.0**	**4.0**	**4.0**	**4.0**	**4.0**
Initial adhesive force	N/cm	**140**	**145**	**144**	**153**	**140**	**152**	**180**
Heat-resistant adhesive force	N/cm	**110**	**108**	**108**	**125**	**112**	**120**	**163**
Fatigue resistance in rubber	%	**48**	**49**	**49**	**54**	**50**	**52**	**71**
Viscosity change rate	V_{30}/V_0	**100**	**98**	**101**	**110**	**120**	**130**	**180**
Generation of aggregate in dipping process	-	B	B	A	A	A	B	S

Claims

1. An adhesive treatment agent for rubber and fiber, the adhesive treatment agent comprising at least:

   a lignin derivative (A);
   a water-soluble or water-dispersible crosslinking agent (B); and
   a rubber latex (C),
   the adhesive treatment agent not comprising a resorcin-formaldehyde resin,
   wherein the lignin derivative (A) has a number average molecular weight of 10,000 to 60,000 and a weight average molecular weight of 80,000 to 130,000.

2. The adhesive treatment agent for rubber and fiber according to claim 1, wherein

   a content of the lignin derivative (A) is 5 to 50 wt% when a total solid content contained in the adhesive treatment agent is 100 wt%,
   a solid content weight ratio of the lignin derivative (A) to the water-soluble or water-dispersible crosslinking agent (B) is (solid content of A) : (solid content of B) = 10 : 1 to 10 : 20, and
   when the adhesive treatment agent is formed into a dry film, the dry film has a maximum point strength of 0.2 MPa to 1.6 MPa, and a maximum point elongation of 2% to 120%.

3. The adhesive treatment agent for rubber and fiber according to claim 1 or 2, wherein the water-soluble or water-dispersible crosslinking agent (B) contains at least one compound selected from the group consisting of an oxazoline group-containing compound, an epoxy compound, and a blocked isocyanate compound.

4. The adhesive treatment agent for rubber and fiber according to any one of claims 1 to 3, wherein the water-soluble or water-dispersible crosslinking agent (B) is an HDI-based blocked isocyanate or an MDI-based oxime blocked isocyanate.

5. The adhesive treatment agent for rubber and fiber according to any one of claims 1 to 4, wherein in the adhesive treatment agent, a solid content weight ratio of the lignin derivative (A) and the water-soluble or water-dispersible crosslinking agent (B) to the rubber latex (C) is ((solid content of A) + (solid content of B)) : (solid content of C) = 10 : 90 to 60 : 40.

6. The adhesive treatment agent for rubber and fiber according to any one of claims 1 to 5, wherein a change rate V_{30}/V_0 of a liquid viscosity (V_{30} (mPa·s)) of the adhesive treatment agent after 30 days with respect to a liquid viscosity (V_0 (mPa·s)) of the adhesive treatment agent after liquid preparation is 90 to 120%.

7. A synthetic fiber cord for rubber reinforcement, the synthetic fiber cord being obtained by adhering the adhesive treatment agent for rubber and fiber according to any one of claims 1 to 6 to a synthetic fiber and performing a heat treatment.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2022/042195

A. CLASSIFICATION OF SUBJECT MATTER

D06M 15/17(2006.01)i; ***D06M 13/395***(2006.01)i; ***D06M 15/356***(2006.01)i; ***D06M 15/55***(2006.01)i; ***D06M 15/693***(2006.01)i
FI: D06M15/17; D06M13/395; D06M15/356; D06M15/55; D06M15/693

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)

D06M13/00-15/715; B29B11/16; B29B15/08-15/14; B60C1/00-19/12; C08J5/04-5/10; C08J5/24; C09J1/00-5/10; C09J9/00-201/10

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2022
Registered utility model specifications of Japan 1996-2022
Published registered utility model applications of Japan 1994-2022

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2001-234143 A (TORAY IND INC) 28 August 2001 (2001-08-28) claims	1-7
A	WO 2018/003572 A1 (NAGASE CHEMTEX CORPORATION) 04 January 2018 (2018-01-04) claims	1-7
A	JP 2021-522386 A (PORCHER INDUSTRIES) 30 August 2021 (2021-08-30) claims, paragraph [0013]	1-7
E, X	JP 2022-177781 A (TORAY IND INC) 01 December 2022 (2022-12-01) claims, examples	1-7
E, X	JP 2022-177782 A (TORAY IND INC) 01 December 2022 (2022-12-01) claims, examples	1-7

☐ Further documents are listed in the continuation of Box C. ☑ 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
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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
"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
"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
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 December 2022	**27 December 2022**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2022/042195

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
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WO 2018/003572 A1	04 January 2018	CN 109196161 A KR 10-2019-0040127 A TW 201823550 A	
JP 2021-522386 A	30 August 2021	US 2021/0115310 A1 claims, paragraph [0017] WO 2019/207141 A1 EP 3784719 A1 FR 3080627 A CN 112135862 A KR 10-2021-0005185 A CA 3098599 A BR 112020021786 A	
JP 2022-177781 A	01 December 2022	(Family: none)	
JP 2022-177782 A	01 December 2022	(Family: none)	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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- JP 2013064037 A **[0012]**
- JP 2020525622 W **[0012]**
- JP 2019518087 W **[0012]**
- WO 2018003572 A **[0012]**
- US 20200024416 A **[0012]**
- JP 2013010909 A **[0012]**