(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 623 668 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
07.08.2013 Bulletin 2013/32

(51) Int Cl.:
D21F 3/02 *(2006.01)*

(21) Application number: **13000526.7**

(22) Date of filing: **01.02.2013**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(30) Priority: **01.02.2012 JP 2012020044**

(71) Applicant: **Ichikawa Co., Ltd.**
Tokyo-to (JP)

(72) Inventors:
- **Yazaki, Takao**
  Tokyo-TO (JP)
- **Yamazaki, Shintaro**
  Tokyo-TO (JP)
- **Takamori, Yuya**
  Tokyo-TO (JP)

(74) Representative: **Müller-Boré & Partner**
Patentanwälte
Grafinger Straße 2
81671 München (DE)

(54) Paper making shoe press belt

(57) A paper making shoe press belt includes a reinforcing fiber substrate and a polyurethane laminate. The reinforcing fiber substrate is embedded in at least one layer of the polyurethane laminate. At least one layer of the polyurethane laminate includes a polyurethane obtained by heat-curing a urethane prepolymer together with a mixed curing agent. The urethane prepolymer includes a terminal isocyanate group and is obtained by reacting a diisocyanate compound and a long-chain polyol. The diisocyanate compound includes at least one of toluene-diisocyanate, diphenylmethane-diisocyanate, and paraphenylene-diisocyanate. The mixed curing agent includes 70-99.5 mol% of dimethylthiotoluenediamine and 0.5-30 mol% of a curing agent The curing agent includes at least one of diethyltoluenediamine and hydroquinone bis β-hydroxyethyl) ether. An equivalent ratio of active hydrogen groups of the mixed curing agent to isocyanate groups of the urethane prepolymer is from 1.02 to 1.15.

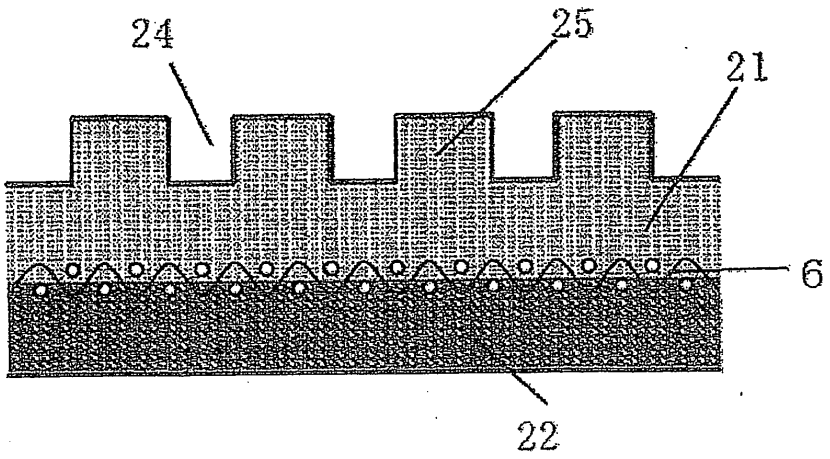

FIG. 1

EP 2 623 668 A1

Description

[0001] This application claims priority to Japanese Patent Application No. 2012-020044, filed February 1, 2012, the disclosure of which is incorporated herein by reference in its entirety.

[0002] In a paper making shoe press device, dehydration is performed by passing a transportation felt 3 and a wet web 4 through a press section formed of a press roll 1 and a shoe 5 using a shoe press mechanism in which a loop-like shoe press belt 2 is provided between the press roll 1 and the shoe 5, as shown, for example, in FIG. 3.

[0003] As shown, for example, in FIG. 1, the shoe press belt 2 includes a outer peripheral polyurethane layer 21 and a inner peripheral polyurethane layer 22 provided on both surfaces of a reinforcing fiber substrate 6, which is integrated into the polyurethane layers. A large number of concave grooves 24 are formed in the press roll side surface of the outer peripheral polyurethane layer 21. Water squeezed from a wet web 4 during pressing is held in the concave grooves 24, and the held water is further transferred to the outside of the press section by the rotation of the belt. Therefore, it is desired that the concave grooves 24 formed in the press roll side surface of the outer peripheral polyurethane layer 21 should have improved shape retention properties when pressurized by a press roll 1 and the shoe 5. It is further desired that a convex part 25 of the press roll side surface of the outer peripheral polyurethane layer 21 be improved in mechanical properties such as cracking resistance, resistance to fatigue from flexing, and wear resistance against vertical pressing force by the press roll 1, the friction of the shoe press belt in a shoe press region, and fatigue from flexing.

[0004] Polyurethanes that exhibit excellent cracking resistance and wear resistance are widely used as resin materials to form the outer peripheral polyurethane layer 21 of the shoe press belt 2.

[0005] For example, JP-A-11-247086 discloses a shoe press belt including an outer peripheral polyurethane layer and an inner peripheral polyurethane layer provided on both surfaces of a reinforcing fiber substrate, which is integrated into the polyurethane layers. The polyurethane of the outer peripheral layer and inner peripheral layer is obtained by heat-curing a urethane prepolymer having a terminal isocyanate group (TAKENATE L2395 manufactured by Takeda Pharmaceutical Company Limited), obtained by reacting toluene-diisocyanate (TDI) with polytetramethylene glycol (PTMG), and 3,3'-dichloro-4,4'-diaminodiphenylmethane (which is a compound commercially available as MBOCA and MOCA and also known as 4,4'-methylene bis-orthochloroaniline or 4,4'-methylene bis-(2-chloroaniline)) as a curing agent (chain extender).

[0006] JP-B-3698984, U.S. Patent No. 7,374,641, EP 0 855 414, JP-B-3803106, and U.S. Patent No. 7,090,747 disclose a shoe press belt including an outer peripheral polyurethane layer and an inner peripheral polyurethane layer provided on both surfaces of a reinforcing fiber substrate, which is integrated into the polyurethane layers. The polyurethane of the outer peripheral layer is obtained by heat-curing a urethane prepolymer having a terminal isocyanate group (HIPREN L manufactured by Mitsui Chemicals, Inc.), obtained by reacting toluene-diisocyanate (TDI) with polytetramethylene glycol (PTMG), and dimethylthiotoluenediamine (ETHACURE 300).

[0007] Dimethylthiotoluenediamine is used instead of 3,3'-dichloro-4,4'-diaminodiphenylmethane as a curing agent in JP-B-3698984, U.S. Patent No. 7,374,641, EP 0 855 414, JP-B-3803106, and U.S. Patent No. 7,090,747 because: (i) JP-A-7-292237 points out the toxicity of 4,4'-methylenebis-(2-chloroaniline) and recommends use of diethyltolylenediamine as a curing agent (see paragraph [0006]), (ii) the journal "Polyfile," January 1999, pp. 37-38, "ETHACURE 300: New Curing Agent as Substitute for MOCA" describes that ETHACURE 300 has excellent low-temperature curability equivalent to that of MOCA and lower toxicity than MOCA, and thus is used as a substitute for MOCA; and (iii) the journal "POLYMER," vol. 36, 1995, pp. 767-774, "The effect of curative on the fracture toughness of PTMEG/TDI polyurethane elastomers" recommends ETHACURE 300 as a substitute for MOCA as a curing agent for a TDI/PTMG-based urethane prepolymer because a polyurethane cured with (ETHACURE 300 is superior in low-temperature curability and crack growth inhibiting effect to a polyurethane cured with MOCA (see FIG. 7 and column "Conclusion").

[0008] JP-A-10-212333 describes both 4,4'-methylenebis-(2-chloroaniline) and dimethylthiotoluenediamine as curing agents for a polyurethane constituting a belt (see claim 17, paragraphs [0011], [0022]).

[0009] "POLYMER," vol. 36, 1995, pp. 767-774, "The effect of curative on the fracture toughness of PTMEG/TDI polyurethane elastomers" indicates, in the results of the crack occurrence resistance test shown in FIG. 7, that "a polyurethane using MOCA has a higher initial tear strength energy than that of a polyurethane using Ethacure 300 but ruptures at this strength whereas the polyurethane using Ethacure 300 has a lower initial crack occurrence tear strength energy than that of the polyurethane using MOCA but does not lead to rupture although experiencing increased occurrence of small cracks for a short time as understood from the results of a subsequent repeated crack test." Results similar to those described above would be expected for a crack occurrence resistance test performed on a shoe press belt having grooves on a surface as shown in the drawings of JP-A-11-247086. In a crack occurrence resistance test performed on a shoe press belt that does not have grooves, a polyurethane prepared using ETHACURE 300 would be expected to have a lower crack occurrence strength energy than that of a polyurethane prepared using MOCA.

[0010] In embodiments, the present invention is directed to a paper making shoe press belt (also referred to as a shoe press belt) used in a paper making shoe press device. In particular embodiments, the present invention is directed to a shoe press belt used in a closed type shoe press. Exemplary shoe press belts according to the present invention are

excellent in cracking resistance. Exemplary shoe press belts according to the present invention include a reinforcing fiber substrate embedded in one or more adjacent polyurethane layers formed from a urethane prepolymer having specific composition that is heat-cured with a mixed chain extender.

[0011] Exemplary shoe press belts according to the present invention exhibit excellent results in a crack occurrence resistance test whether the belts include or do not include grooves in an outermost surface. Exemplary shoe press belts according to the present invention may be prepared using both ETHACURE 300 as a main component and another curing agent having excellent low-temperature curability as a subcomponent, as curing agents employed to completely cure a urethane prepolymer.

[0012] In exemplary embodiments of the present invention a paper making shoe press belt includes a reinforcing fiber substrate and a polyurethane laminate. In a preferred embodiment, the polyurethane laminate is integrally constituted. The reinforcing fiber substrate is embedded in at least one layer of the polyurethane laminate. At least one layer of the polyurethane laminate includes a polyurethane obtained by heat-curing a urethane prepolymer (A) together with a mixed curing agent (B). The urethane prepolymer (A) includes a terminal isocyanate group. The urethane prepolymer (A) is obtained by reacting a diisocyanate compound (a) and a long-chain polyol (b). The diisocyanate compound (a) includes at least one of toluene-diisocyanate (TDI), diphenylmethane-diisocyanate (MDI), and paraphenylene-diisocyanate (PPDI). The mixed curing agent (B) includes 70-99.5 mol% of dimethylthiotoluenediamine (c) and 0.5-30 mol% of a curing agent (d). The curing agent (d) includes at least one of diethyltoluenediamine and hydroquinone bis (β-hydroxyethyl) ether (hereinafter may be referred to as hydroquinone bis-β hydroxylethyl ether). An equivalent ratio of active hydrogen groups of the mixed curing agent (B) to isocyanate groups of the urethane prepolymer (A) ((-H)/(-NCO)) is from 1.02 to 1.15.

[0013] In one embodiment of the present invention, a paper making shoe press belt is formed of a polyurethane, wherein a reinforcing fiber substrate is integrated with polyurethane layers and the reinforcing fiber substrate is buried in the polyurethane, wherein the polyurethane is obtained by heat-curing a urethane prepolymer (A) having a terminal isocyanate group, obtained by reacting
a diisocyanate compound (a) selected from toluene-diisocyanate (TDI), diphenylmethane-diisocyanate (MDI), and paraphenylene-diisocyanate (PPDI) with
a long-chain polyol (b), and
a mixed curing agent (B) comprising
70-99.5 mol% of dimethylthiotoluenediamine (c) and
0.5-30 mol% of a curing agent (d) selected from diethyltoluenediamine and hydroquinone bis-β hydroxylethyl ether, and wherein the equivalent ratio (-H/-NCO) of an active hydrogen group (-H) of the mixed curing agent to the isocyanate group (-NCO) of the urethane prepolymer (A) is 1.02-1.15.

[0014] In embodiments of the shoe press belt according to the present invention, because an outer peripheral polyurethane layer of the shoe press belt facing a wet web side is formed from a polyurethane that is completely cured with a mixed curing agent, the shoe press belt exhibits improved results in a crack occurrence resistance test.

[0015] A more complete appreciation of the invention and many of the attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

[0016] FIG. 1 is a cross-sectional view of an exemplary shoe press belt;

[0017] FIG. 2 is a cross-sectional view of an exemplary shoe press belt;

[0018] FIG. 3 is a cross-sectional view of an exemplary shoe press device;

[0019] FIG. 4 is a schematic depiction of a test for crack propagation properties using a De Mattia flex tester; and

[0020] FIG. 5 is a schematic depiction of a test for measuring crack occurrence in a shoe press belt.

[0021] Referring now to the drawings, wherein like reference numerals designate identical or corresponding parts throughout the several views, exemplary embodiments of the present invention will be described in more detail. The present invention is not limited to the exemplary embodiments shown in the drawings.

[0022] FIG. 1 is a cross-sectional view of an exemplary shoe press belt 2 according to the present invention, in which a reinforcing fiber substrate 6 is integrated with a polyurethane in an outer peripheral layer 21 and an inner peripheral layer 22. The reinforcing fiber substrate 6 is embedded in the polyurethane, and grooves 24 are formed in the outer peripheral polyurethane layer 21.

[0023] FIG. 2 illustrates an alternative exemplary embodiment of the present invention, in which grooves 24 are not formed in an outer peripheral polyurethane layer. FIG. 2(a) shows a configuration in which a reinforcing fiber substrate 6 is embedded at the interface of an outer peripheral polyurethane layer 2a and an inner peripheral polyurethane layer 2b, the layers being of like composition. FIG. 2(b) shows a configuration in which a reinforcing fiber substrate 6 is embedded at the interface of an outer peripheral polyurethane layer 2a and an inner peripheral polyurethane layer 2b, the layers being of different composition. FIG. 2(c) shows a configuration in which a reinforcing fiber substrate 6 is embedded in an intermediate polyurethane layer 2c provided between an outer peripheral polyurethane layer 2a and an inner peripheral polyurethane layer 2b.

[0024] FIG. 3 is a simplified diagram of a shoe press mechanism in a paper making machine. In the figure, reference numeral 2 denotes a shoe press belt, reference numeral 4 denotes a wet web, reference numeral 3 denotes a paper-making felt, reference numeral 1 denotes a press roll, and reference numeral 5 denotes a shoe.

[0025] FIG. 4 is an explanatory drawing showing conduct of a test for crack propagation properties of a polyurethane test piece 61 using a De Mattia flex tester.

[0026] FIG. 5 is an explanatory drawing of a tester 42 for measuring crack occurrence in a shoe press belt 41.

[0027] In various exemplary embodiments, the reinforcing fiber substrate 6 may be a woven fabric as described in JP-A-11-247086, U.S. Patent No. 7,374,641, or EP 0 855 414, or alternative reinforcing fiber substrates described in other documents. For example, the reinforcing fiber substrate 6 may be a grid-like material in which 5000 dtex multifilament twisted yarns of polyethylene terephthalate (PET) fibers are used as warp and weft, the warp is sandwiched in the weft, and the intersections between the weft and the warp are bonded by polyurethane adhesion. As fiber materials, polyamide fibers such as fibers of aramid, nylon 6,6, nylon 6,10, and nylon 6 may be used instead of polyethylene terephthalate fibers. Further, fibers made of different materials may be used for the warp and the weft, or warp and weft having different thicknesses like 5000 dtex and 7000 dtex may be used.

[0028] In various exemplary embodiments, the polyurethane that forms the outer peripheral polyurethane layer 21 of the shoe press belt is a polyurethane with a JIS-A hardness of 90 to 99, preferably 94 to 97, obtained by heat-curing a urethane prepolymer (A) having a terminal isocyanate group, obtained by reacting (a) a diisocyanate compound selected from toluene-diisocyanate (TDI), diphenylmethane-diisocyanate (MDI), and paraphenylene-diisocyanate (PPDI) with (b) a long-chain polyol, and a mixed curing agent (B) comprising (c) 70-99.5 mol% of dimethylthiotoluenediamine and (d) 0.5-30 mol% of a curing agent selected from diethyltoluenediamine and hydroquinone bis (β-hydroxyethyl) ether, wherein the equivalent ratio (-H/-NCO) of active hydrogen groups (-H) of the mixed curing agent to isocyanate groups (-NCO) of the urethane prepolymer (A) is 1.02-1.15.

[0029] In various exemplary embodiments, the polyurethane that forms the inner peripheral polyurethane layer 22 of the shoe press belt may be identical to the polyurethane that forms the outer peripheral polyurethane layer 21 or may be a polyurethane having different composition.

[0030] In various exemplary embodiments, the long-chain polyol which is the raw material of the urethane prepolymer (A), may include one or two or more polyol compounds selected from polyether polyols, polyester polyols, polycaprolactone polyols, and polycarbonate polyols. In some such embodiments, polytetramethylene glycol (PTMG), polyethylene glycol (PEG), an addition product of ethylene oxide with propylene oxide, propylene glycol (PPG), and/or the like may be used.

[0031] In various exemplary embodiments, the shoe press belt is manufactured by a method in which a mandrel surface coated with a mold release agent is coated and impregnated with a mixture of a urethane prepolymer and a mixed curing agent for forming an inner peripheral polyurethane layer while rotating the mandrel so that the inner peripheral polyurethane layer is formed to a thickness of 0.8-3.5 mm on a mandrel surface. The resulting layer is pre-cured at 85-125°C for 0.5-1 hour. A reinforcing fiber substrate is wound therearound and a mixture of a urethane prepolymer and a curing agent for forming an intermediate layer is then coated to a thickness of 0.5-2 mm. The reinforcing fiber substrate is impregnated with the mixture which also adheres to the inner peripheral polyurethane layer, and the resulting layer is pre-cured at 50-120°C for 0.5-1 hour. Thereafter, the surface of the reinforcing fiber substrate is coated and impregnated with a mixture of a urethane prepolymer and a curing agent for forming an outer peripheral polyurethane layer while rotating the mandrel so that the outer peripheral polyurethane layer is formed to a thickness of 1.5-4 mm. The resulting structure is cured at 100-130°C for 2-20 hours. Thereafter, grooves as illustrated in FIG. 1 are carved into the outer peripheral polyurethane layer. The grooves may be carved into the outer peripheral polyurethane layer by bringing a heated emboss roll having a surface with protrusions having heights of groove depths into pressure contact with the outer peripheral polyurethane layer during curing of the outer peripheral polyurethane layer. The mandrel includes a heating apparatus.

[0032] In alternative embodiments, the shoe press belt is manufactured by a method in which a mandrel surface coated with a mold release agent is coated with a mixture of a urethane prepolymer and a mixed curing agent for forming an inner peripheral polyurethane layer so that the inner peripheral polyurethane layer is formed to a thickness of 0.8-3 mm. The resulting layer is pre-cured at 70-130°C for 0.5-2 hours. A reinforcing fiber substrate is then wound around the external surface of the inner peripheral polyurethane layer and a mixture of a urethane prepolymer and a curing agent for forming an intermediate layer is coated to a thickness of 0.5-2 mm. The reinforcing fiber substrate is impregnated with the mixture, which also adheres to the inner peripheral polyurethane layer. The resulting layer is pre-cured at 50-120°C for 0.5-1 hour. A mixture of a urethane prepolymer and a mixed curing agent for forming an outer peripheral polyurethane layer is coated so that the outer peripheral polyurethane layer has a thickness of 2-4 mm. The resulting structure is cured at 70-130°C for 12-20 hours. Grooves are cut and processed in the outer peripheral polyurethane layer with a cutting tool, and the outer peripheral polyurethane layer is polished with sandpaper or a polyurethane abrasive cloth.

[0033] In alternative embodiments, the shoe press belt is manufactured by a method in which a mandrel surface coated

with a mold release agent is coated with a mixture of a urethane prepolymer and a curing agent for forming an inner peripheral polyurethane layer so that the inner peripheral polyurethane layer is formed to a thickness of 0.8-3 mm. The resulting layer is pre-cured at 50-140°C for 0.5-2 hours. An intermediate polyurethane layer having a thickness of 1-2 mm in which a reinforcing fiber substrate is embedded (produced beforehand) is wound around the outer surface of the inner peripheral polyurethane layer. The intermediate layer is pressed by a nip roll heated to 50-140°C. A mixture of a urethane prepolymer and a mixed curing agent for forming an outer peripheral polyurethane layer is further coated so that the outer peripheral polyurethane layer is formed to a thickness of 2-4 mm. The resulting structure is cured at 70-140°C for 2-20 hours. The outer peripheral polyurethane layer is polished with sandpaper or a polyurethane abrasive cloth. Grooves are cut and processed in the polished outer peripheral polyurethane layer with a cutting tool.

[0034] In alternative embodiments, the shoe press belt is manufactured by a method using two rolls instead of a mandrel. For example, an endless reinforcing fiber substrate is extended between two rolls. The surface of the reinforcing fiber substrate is coated with a mixture of a urethane prepolymer and a curing agent. The reinforcing fiber substrate is impregnated with the mixture and the resulting structure is pre-cured at 50-120°C for 0.5-2 hours. A mixture of a urethane prepolymer and a mixed curing agent for forming an inner peripheral polyurethane layer is coated onto the reinforcing fiber substrate so that the inner peripheral polyurethane layer is formed to a thickness of 0.5-3 mm. The resulting structure is pre-cured at 70-140°C for 2-12 hours. A surface of the inner peripheral polyurethane layer is polished with sandpaper or an abrasive cloth. The semifinished product is reversed, hung on the two rolls, and extended. The surface of the extended semifinished product is coated with a mixture of a urethane prepolymer and a mixed curing agent for forming an outer peripheral polyurethane layer to impregnate the reinforcing fiber substrate. The surface of the extended semifinished product is further coated with the mixture so that the outer peripheral polyurethane layer is formed to a thickness of 1.5-4 mm. The resulting structure is cured at 70-140°C for 2-20 hours. After curing, the outer peripheral polyurethane layer is polished to a predetermined thickness, and grooves are cut and processed in the outer peripheral polyurethane layer with a cutting tool.

EXAMPLES

[0035] In the following examples, and throughout this specification, all parts and percentages are by weight, and all temperatures are in degrees Celsius, unless expressly stated to be otherwise. Where the solids content of a dispersion or solution is reported, it expresses the weight of solids based on the total weight of the dispersion or solution, respectively. Where a molecular weight is specified, it is the molecular weight range ascribed to the product by the commercial supplier, which is identified. Generally this is believed to be weight average molecular weight.

[0036] In order to evaluate the physical properties of polyurethane that forms a shoe press belt, polyurethane test pieces were produced as described below.

[0037] Reference Example 1 (Example 1)

[0038] A urethane prepolymer (percentage of NCO: 6.02%, viscosity at 80°C: 400 cps, preheat temperature: 100°C) obtained by reacting toluene-diisocyanate (TDI) with polytetramethylene glycol (PTMG) and a mixed curing agent consisting of 90 mol% of dimethylthiotoluenediamine (ETHACURE 300) and 10 mol% of hydroquinone bis (β-hydroxyethyl) ether (HQEE) (H/NCO ratio of the mixed curing agent to the urethane prepolymer would be 1.05) were poured into a preheated die, heated to 115°C, precured at 115°C for 0.5 hour, then removed from the die, and post-cured at 115°C for 16 hours to obtain a polyurethane sheet. A test piece (thickness of 3.5 mm) was produced from the sheet.

[0039] Reference Example 6 (Comparative Example 1)

[0040] A urethane prepolymer (percentage of NCO: 6.02%, viscosity at 80°C: 400 cps, preheat temperature: 66°C) obtained by reacting toluene-diisocyanate (TDI) with polytetramethylene glycol (PTMG) and a curing agent composed of dimethylthiotoluenediamine (ETHACURE 300) (H/NCO ratio of the mixed curing agent to the urethane prepolymer would be 0.95) were poured into a preheated die, heated to 100°C, precured at 100°C for 0.5 hour, then removed from the die, and post-cured at 100°C for 16 hours to obtain a polyurethane sheet. A test piece (thickness of 3.5 mm) was produced from the sheet.

[0041] Reference Examples 2-5 (Examples 2-5) and Reference Examples 7-11 (Comparative Examples 2-6)

[0042] Polyurethane sheets were obtained in the same manner as in Reference Example 1 except that urethane prepolymers listed in TABLE 1 and TABLE 2 as urethane prepolymers and curing agents listed in TABLE 1 and TABLE 2 as curing agents were used at H/NCO ratios listed in the tables and under preheating and curing conditions listed in the tables. Test pieces (thicknesses of 3.5 mm) were produced from the sheets.

[0043] The curing agents listed in TABLE 1 and TABLE 2 are dimethylthiotoluenediamine (ETHACURE 300), diethyltoluenediamine (ETHACURE 100), hydroquinone bis (β-hydroxylethyl) ether (HQEE, BHEB), and 4,4'-methylenebis-(2-chloroaniline) (MOCA).

[0044] The polyurethane sheet test pieces obtained in Examples 1-11 were subjected to a De Mattia flex test. In the flex test, a test for crack propagation properties was conducted using a tester, illustrated in FIG. 4, similar to that in the De Mattia flex test defined in JIS-K-6260 (2005) under an atmosphere at 20°C and a relative humidity of 52% under the

following conditions. The test piece 61 had a width of 25 mm, a length of 185 mm (including one side of tong hold of 20 mm), a length of 150 mm between grippers 62, a thickness of 3.4 mm, and a semicircular dimple 61 a having a radius of 1.5 mm in a center. In reciprocating motion, the maximum distance between the grippers was 100 mm, the minimum distance was 35 mm, a motion distance was 65 mm, and a reciprocation speed was 360 reciprocations/min. A slit having a length of about 2 mm was notched in the center of the test piece in a width direction. The right and left grippers were set to be at angles of 45° with respect to a reciprocation direction, respectively. Flexing was repeated under the foregoing conditions and crack length was measured after predetermined increments of strokes. The number of strokes as used herein was a value obtained by multiplying test time by reciprocation speed. The test was finished when the crack length exceeded 15 mm from a measurement value of an early notch length (about 2 mm), an approximate curve of the number of strokes and the crack length was drawn, the number of strokes was read when the crack length was 15 mm, and a value obtained by dividing a growing crack length (15 mm in crack length - measurement value of marly notch length) by the number of strokes at this time was regarded as a crack propagation property. The obtained physical properties are summarized in TABLE 1 and TABLE 2.

[0045]

TABLE 1

	Reference Example 1	Reference Example 2	Reference Example 3	Reference Example 4	Reference Example 5
	Example 1	Example 2	Example 3	Example 4	Example 5
Urethane prepolymer					
Isocyanate	TDI	TDI	PPDI	PPDI/MDI 9/1	MDI
Polyol	PTMG	PTMG	PTMG	PTMG	PTMG
NCO (%)	6.02	6.02	5.51	5.84	8.85
Viscosity (cps)	400 (@80°C)	400 (@80°C)	1800 (@55°C)	1800 (@55°C)	400 (@100°C)
Preheat temperature (°C)	100	100	66	80	100
Curing agent (compound name)	ETHACURE 300	ETHACURE 300	ETHACURE 300	ETHACURE 300	ETHACURE 300
Equivalent value	107.15	107.15	107.15	107.15	107.15
Active hydrogen (mol%)	90	90	99.5	98	70
Preheat temperature (°C)	50	50	24	24	24
Curing agent (compound name)	HQEE	HQEE	ETHACURE 100	ETHACURE 100	HQEE
Equivalent value	99.11	99.11	89.14	89.14	99.11
Activehydrogen (mol%)	10	10	0.5	2	30
Preheat temperature (°C)	130	130	24	24	130

(continued)

	Reference Example 1	Reference Example 2	Reference Example 3	Reference Example 4	Reference Example 5
	Example 1	Example 2	Example 3	Example 4	Example 5
Equivalent value of curing agent	106.35	106.35	107.06	106.79	104.74
Equivalent ratio (H/NCO ratio)	1.05	1.15	1.02	1.10	1.10
Blending of curing agent (parts)	16.0	17.5	14.3	16.3	24.3
Precuring condition (°C/hr)	115/0.5	115/0.5	127/0.5	127/0.5	115/1
Post-curing condition (°C/hr)	115/16	115/16	127/16	127/16	115/16
Crack propagation property (μm/time)	0.99	0.22	0.30	0.43	1.06

TABLE 2

	Reference Example 6	Reference Example 7	Reference Example 8	Reference Example 9	Reference Example 10	Reference Example 11
	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6
Urethane prepolymer						
Isocyanate	TDI	TDI	TDI	TDI	MDI	TDI/MDI 5/5
Polyol	PTMG	PTMG	PTMG	PTMG	PTMG	PTMG
NCO (%)	6.02	6.02	6.02	6.02	8.85	7.44
Viscosity (cps)	400 (@80°C)	400 (@80°C)	400 (@80°C)	400 (@80°C)	400 (@100°C)	600 (@80°C)
Preheat temperature (°C)	66	66	66	66	80	66
Curing agent (compound name)	ETHACURE 300	ETHACURE 300	MOCA	MOCA	ETHACURE 300	ETHACURE 300
Equivalent value	107.15	107.15	133.6	133.6	107.15	107.15
Active hydrogen (mol%)	100	100	100	100	100	100
Preheat temperature (°C)	24	24	116	116	24	24
Curing agent (compound name)						
Equivalent value						
Active hydrogen (mol%)						
Preheat temperature (°C)						
Equivalent value of curing agent	107.15	107.15	133.60	133.60	107.15	107.15
Equivalent ratio (H/NCO ratio)	0.95	1.05	0.95	1.05	1.00	0.95
Blending of curing agent (parts)	14.6	16.1	18.2	20.1	22.6	18.0
Precuring condition (°C/hr)	100/0.5	100/0.5	100/0.5	100/0.5	100/1	115/1
Post-curing condition (°C/hr)	100/16	100/16	100/16	100/16	100/14	115/16
Crack propagation property (μm/time)	6.09	1.53	8.10	2.15	1.41	5.06

[0046] From TABLE 1 and TABLE 2, it is apparent that the polyurethanes of the Examples exhibit better crack propagation resistance than the polyurethanes of the Comparative Examples.

[0047] Shoe press belts were prepared using the polyurethane compositions described above in the manner described

below.

[0048] [Example 1]

[0049] Step 1: A release agent (KS-61: manufactured by Shin-Etsu Chemical Co.; Ltd.) was coated on the surface of a mandrel having a diameter of 1500 mm and that was rotatable by driving means. Then, a composition prepared by mixing the urethane prepolymer (TDI/PTMG-based prepolymer) and the mixed curing agent as specified in Reference Example 1 was spirally coated onto the rotating mandrel to a thickness of 1.4 mm using an injection molding nozzle movable in parallel to the rotation axis of the mandrel, and a urethane resin layer was formed. The layer was left to stand at room temperature for 40 minutes while rotating the mandrel, and the resin was further heated at 115°C for 0.5 hour by a heating apparatus attached to the mandrel and precured to produce a shoe side inner peripheral polyurethane layer.

[0050] Step 2: A grid-like material was prepared using a 5000 dtex multifilament twisted yarn of polyethylene terephthalate fibers as weft and a 550 dtex multifilament yarn of polyethylene terephthalate fibers as warp. The warp was sandwiched in the weft, and the intersections between the weft and the warp were bonded by urethane-based resin adhesion (warp density of 1 strand/cm; and weft density of 4 strands/cm). One layer of the grid-like material having a plurality of pieces was placed on the outer periphery of the shoe side layer without any gap so that the weft was along the axial direction of the mandrel. 6700 dtex multifilament yarn of polyethylene terephthalate fibers was helically wound around the outer periphery of the grid-like material at a pitch of 30 strands/5 cm to form a spool layer. Then, the polyurethane composition was coated to a thickness of about 1.6 mm and integrated as an intermediate layer to fill the gap between the grid-like material and the spool layer, and a reinforcing fiber substrate polyurethane intermediate layer was formed.

[0051] Step 3: A composition prepared by mixing the urethane prepolymer and the curing agent as specified in Reference Example 1 was impregnated and coated to a thickness of about 2.5 mm on the intermediate layer by spiral coating, heated at 115°C for 16 hours, and post-cured to produce an outer peripheral layer. The surface of the outer peripheral layer was polished to have an overall thickness of 5.2 mm, and a shoe press belt was obtained by forming a large number of concave grooves (of 1.0 mm in groove width, 1.0 mm in depth, and 3.18 mm in pitch width) in the machine direction of the belt by a rotary blade.

[0052] [Comparative Example 1]

[0053] A shoe press belt was obtained in the same manner as in Example 1 except that the polyurethane composition used in Reference Example 6 was used instead of the polyurethane composition in Reference Example 1 and the curing conditions of precuring and post-curing were changed to 100°C for 0.5 hour and 100°C for 16 hours, respectively.

[0054] [Example 2] to [Example 5], [Comparative Example 2] to [Comparative Example 6]

[0055] Shoe press belts were obtained in the same manner as in Example 1 except that the urethane prepolymers listed in TABLE 1 and TABLE 2 as urethane prepolymers and the curing agents listed in TABLE 1 and TABLE 2 as curing agents were used under the preheating and curing conditions listed in the tables.

[0056] A flexing fatigue test was conducted for the obtained shoe press belts. The flexing fatigue test was conducted by evaluating the grooved belt samples. As the flexing fatigue test, a crack occurrence test was conducted under an atmosphere of 20°C and a relative humidity of 52% using the device illustrated in FIG. 5. The test piece 71 had a width of 60 mm and a length between grippers of 70 mm. By subjecting a lower gripper 42a to circular-arc reciprocating motion, an upper gripper 42b and the test piece also reciprocated along a circular-arc path so that the test piece was flexed to cause fatigue on the top of the lower gripper. A distance between the center of the circular arc and the top of the lower gripper was 168 mm, the migration length of the lower gripper was 161 mm, and a reciprocation speed was 162 reciprocations/min. The weight of the upper gripper was 400 g. Flexing was repeated under the conditions specified, and the number of flexings until a crack occurred was measured. All the shoe press belts according to Examples exhibited the results in which 1 million flexings could be born. The results are listed in TABLE 3 and TABLE 4.

TABLE 3

	Example 1	Example 2	Example 3	Example 4	Example 5
Number of flexings (ten thousand times)	100 (not cracked)	100 (not cracked)	100 (not cracked)	100 (not cracked)	100 (not cracked)

TABLE 4

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6
Number of flexings (ten thousand times)	20	80	15	56	50	35

[0057] As is evident from the foregoing results, shoe press belts according to embodiments of the present invention (e.g., as in the Examples) are excellent in low-temperature curing properties, exhibit improved crack occurrence inhibiting effect, and have excellent practical values in comparison with known shoe press belts (e.g., as in the Comparative Examples).

[0058] Where a numerical limit or range is stated herein, the endpoints are included. Also, all values and subranges within a numerical limit or range are specifically included as if explicitly written out.

[0059] Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

[0060] All patents and other references mentioned above are incorporated in full herein by this reference, the same as if set forth at length.

[0061] According to the specific embodiment, the present invention is provided as the following (1) to (20).

[0062]

(1) A paper making shoe press belt, comprising:

a reinforcing fiber substrate; and
a polyurethane laminate;
wherein:

the reinforcing fiber substrate is embedded in at least one layer of the polyurethane laminate;
at least one layer of the polyurethane laminate comprises a polyurethane obtained by heat-curing a urethane prepolymer (A) together with a mixed curing agent (B);
the urethane prepolymer (A) comprises a terminal isocyanate group;
the urethane prepolymer (A) is obtained by reacting a diisocyanate compound (a) and a long-chain polyol (b);
the diisocyanate compound (a) comprises at least one member selected from the group consisting of toluene-diisocyanate (TDI), diphenylmethane-diisocyanate (MDI), and paraphenylene-diisocyanate (PPDI);
the mixed curing agent (B) comprises 70-99.5 mol% of dimethylthiotoluenediamine (c) and 0.5-30 mol% of a curing agent (d);
the curing agent (d) comprises at least one member selected from the group consisting of diethyltoluene-diamine and hydroquinone bis (β-hydroxyethyl) ether; and
an equivalent ratio of active hydrogen groups of the mixed curing agent (B) to isocyanate groups of the urethane prepolymer (A) ((-H)/(-NCO)) is from 1.02 to 1.15.

[0063] (2) The paper making shoe press belt of (1), wherein the polyurethane laminate comprises an inner peripheral polyurethane layer and an outer peripheral polyurethane layer.

[0064] (3) The paper making shoe press belt of (2), wherein the inner peripheral polyurethane layer comprises the polyurethane obtained by heat-curing the urethane prepolymer (A) together with the mixed curing agent (B).

[0065] (4) The paper making shoe press belt of (3), wherein the outer peripheral polyurethane layer has a surface comprising grooves.

[0066] (5) The paper making shoe press belt of (3), wherein both the inner peripheral polyurethane layer and the outer peripheral polyurethane layer comprise the polyurethane obtained by heat-curing the urethane prepolymer (A) together with the mixed curing agent (B).

[0067] (6) The paper making shoe press belt of (5), wherein the outer peripheral polyurethane layer has a surface comprising grooves.

[0068] (7) The paper making shoe press belt of (2), wherein the outer peripheral polyurethane layer comprises the polyurethane obtained by heat-curing the urethane prepolymer (A) together with the mixed curing agent (B).

[0069] (8) The paper making shoe press belt of (7), wherein the outer peripheral polyurethane layer has a surface comprising grooves.

[0070] (9) The paper making shoe press belt of any one of (2) to (8), wherein the reinforcing fiber substrate is embedded in both the inner peripheral polyurethane layer and the outer peripheral polyurethane layer.

[0071] (10) The paper making shoe press belt of any one of (2) to (8), further comprising an intermediate polyurethane layer between the inner peripheral polyurethane layer and the outer peripheral polyurethane layer.

[0072] (11) The paper making shoe press belt of (10), wherein the reinforcing fiber substrate is embedded in the intermediate polyurethane layer.

[0073] (12) The paper making shoe press belt of any one of (1) to (11), wherein the diisocyanate compound (a) comprises toluene-diisocyanate (TDI).

[0074] (13) The paper making shoe press belt of any one of (1) to (12), wherein the diisocyanate compound (a) comprises diphenylmethane-diisocyanate (MDI).

[0075] (14) The paper making shoe press belt of any one of (1) to (13), wherein the diisocyanate compound (a) comprises paraphenylene-diisocyanate (PPDI).

[0076] (15) The paper making shoe press belt of any one of (1) to (14), wherein the curing agent (d) comprises diethyltoluenediamine.

[0077] (16) The paper making shoe press belt of any one of (1) to (15), wherein the curing agent (d) comprises hydroquinone bis (β-hydroxyethyl) ether.

[0078] (17) The paper making shoe press belt of any one of (1) to (16), wherein an equivalent ratio of active hydrogen groups of the mixed curing agent (B) to isocyanate groups of the urethane prepolymer (A) is from 1.05 to 1.12.

[0079] (18) The paper making shoe press belt of any one of (1) to (16), wherein an equivalent ratio of active hydrogen groups of the mixed curing agent (B) to isocyanate groups of the urethane prepolymer (A) is from 1.02 to 1.10.

[0080] (19) The paper making shoe press belt of any one of (1) to (16), wherein an equivalent ratio of active hydrogen groups of the mixed curing agent (B) to isocyanate groups of the urethane prepolymer (A) is from 1.10 to 1.15.

[0081] (20) The paper making shoe press belt of any one of (1) to (19), wherein the at least one layer of the polyurethane laminate has a surface comprising grooves.

Claims

1. A paper making shoe press belt, comprising:

a reinforcing fiber substrate; and
a polyurethane laminate;
wherein:

the reinforcing fiber substrate is embedded in at least one layer of the polyurethane laminate;
at least one layer of the polyurethane laminate comprises a polyurethane obtained by heat-curing a urethane prepolymer (A) together with a mixed curing agent (B);
the urethane prepolymer (A) comprises a terminal isocyanate group;
the urethane prepolymer (A) is obtained by reacting a diisocyanate compound (a) and a long-chain polyol (b);
the diisocyanate compound (a) comprises at least one member selected from the group consisting of toluene-diisocyanate (TDI), diphenylmethane-diisocyanate (MDI), and paraphenylene-diisocyanate (PPDI);
the mixed curing agent (B) comprises 70-99.5 mol% of dimethylthiotoluenediamine (c) and 0.5-30 mol% of a curing agent (d);
the curing agent (d) comprises at least one member selected from the group consisting of diethyltoluene-diamine and hydroquinone bis (β-hydroxyethyl) ether; and
an equivalent ratio of active hydrogen groups of the mixed curing agent (B) to isocyanate groups of the urethane prepolymer (A) ((-H)/(-NCO)) is from 1.02 to 1.15.

2. The paper making shoe press belt of claim 1, wherein the polyurethane laminate comprises an inner peripheral polyurethane layer and an outer peripheral polyurethane layer.

3. The paper making shoe press belt of claim 2, wherein the inner peripheral polyurethane layer comprises the polyurethane obtained by heat-curing the urethane prepolymer (A) together with the mixed curing agent (B).

4. The paper making shoe press belt of claim 3, wherein both the inner peripheral polyurethane layer and the outer peripheral polyurethane layer comprise the polyurethane obtained by heat-curing the urethane prepolymer (A)

together with the mixed curing agent (B).

5. The paper making shoe press belt of claim 2, wherein the outer peripheral polyurethane layer comprises the polyurethane obtained by heat-curing the urethane prepolymer (A) together with the mixed curing agent (B).

6. The paper making shoe press belt of claim 2, wherein the reinforcing fiber substrate is embedded in both the inner peripheral polyurethane layer and the outer peripheral polyurethane layer.

7. The paper making shoe press belt of claim 2, further comprising an intermediate polyurethane layer between the inner peripheral polyurethane layer and the outer peripheral polyurethane layer.

8. The paper making shoe press belt of claim 7, wherein the reinforcing fiber substrate is embedded in the intermediate polyurethane layer.

9. The paper making shoe press belt of claim 1, wherein the at least one layer of the polyurethane laminate has a surface comprising grooves.

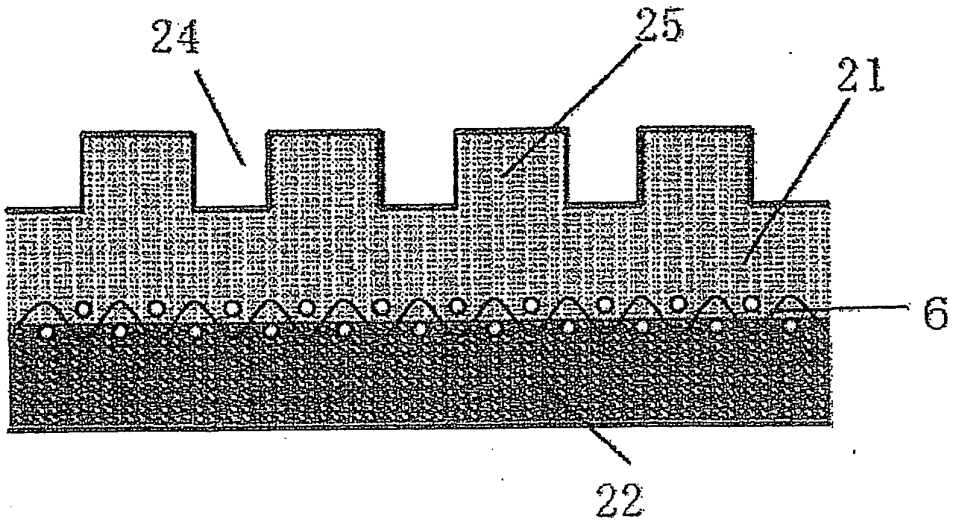

FIG. 1

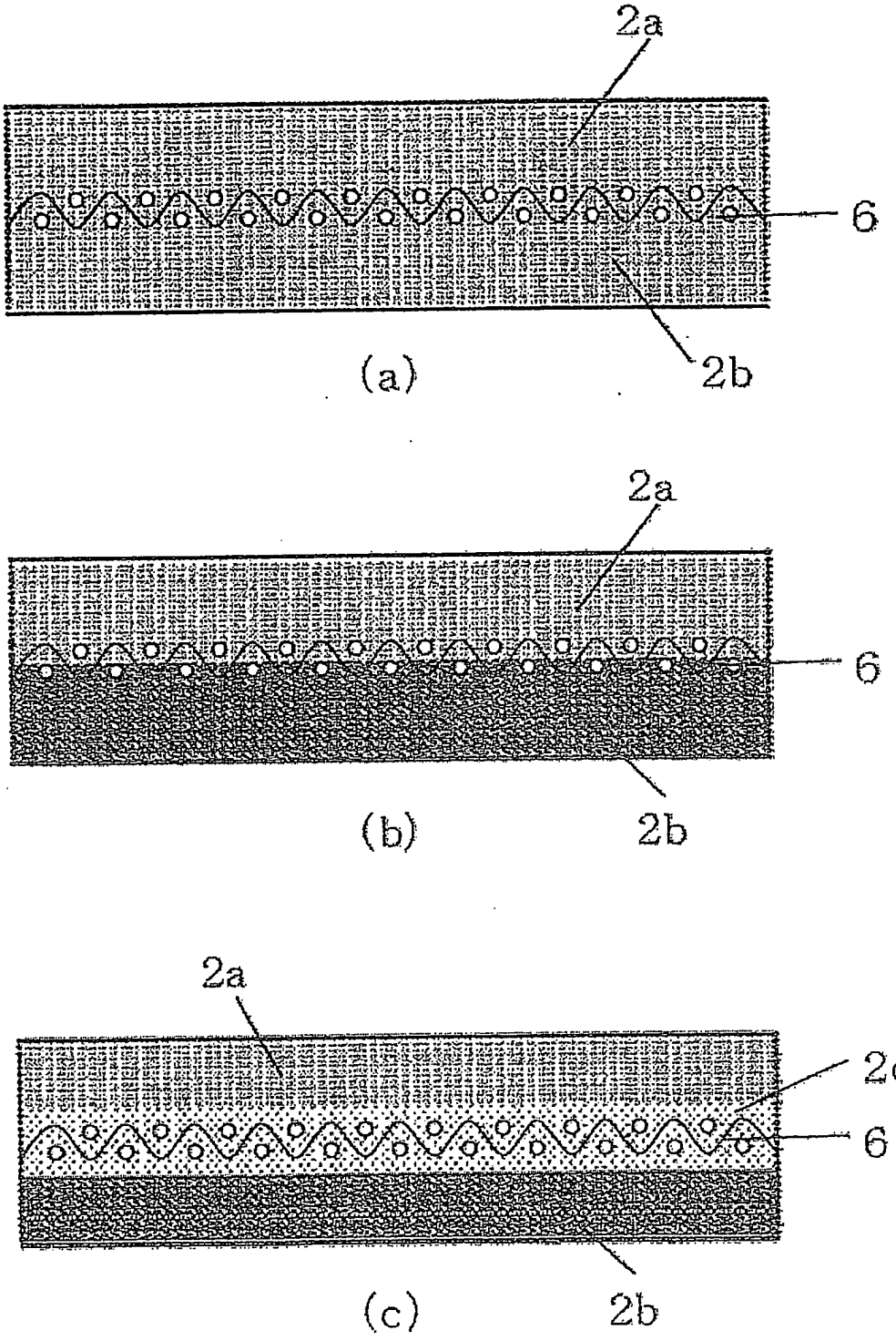

FIG. 2

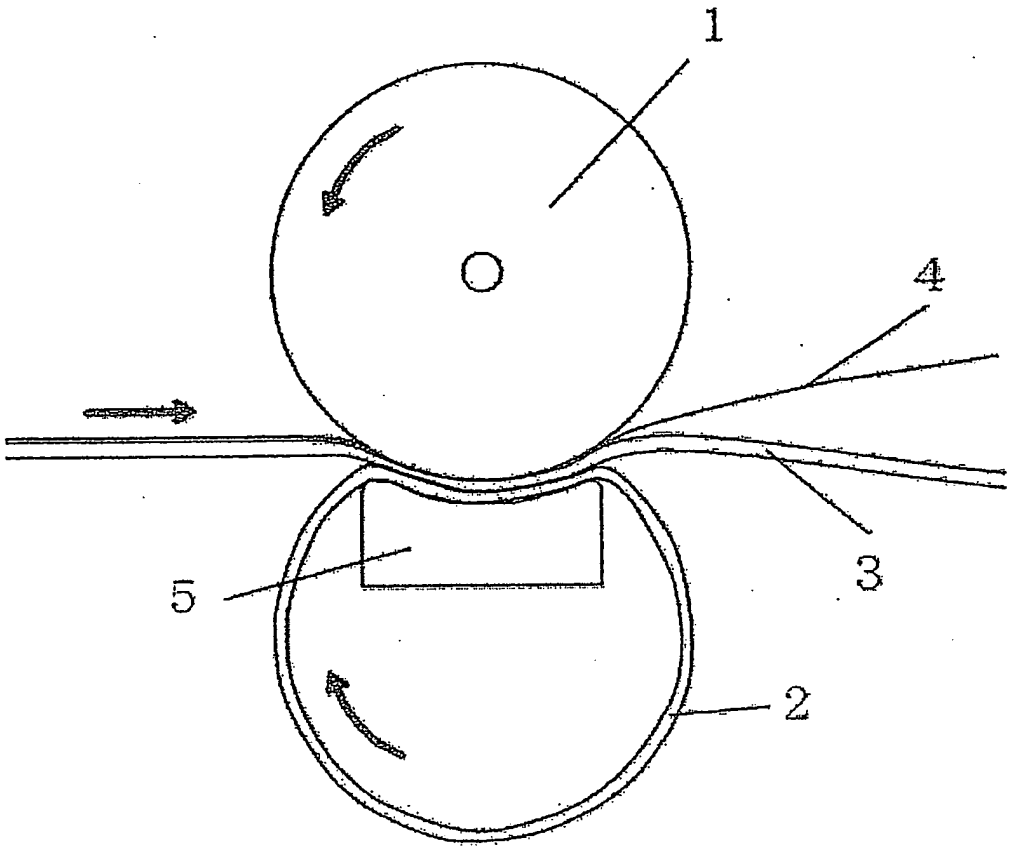

FIG. 3

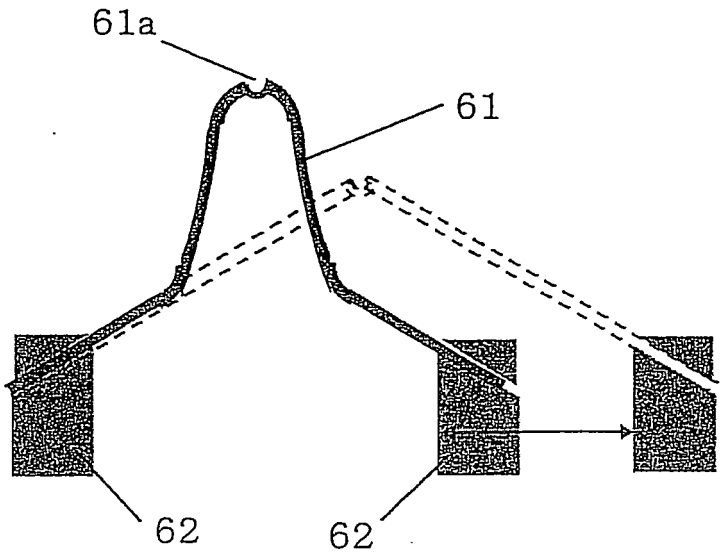

FIG. 4

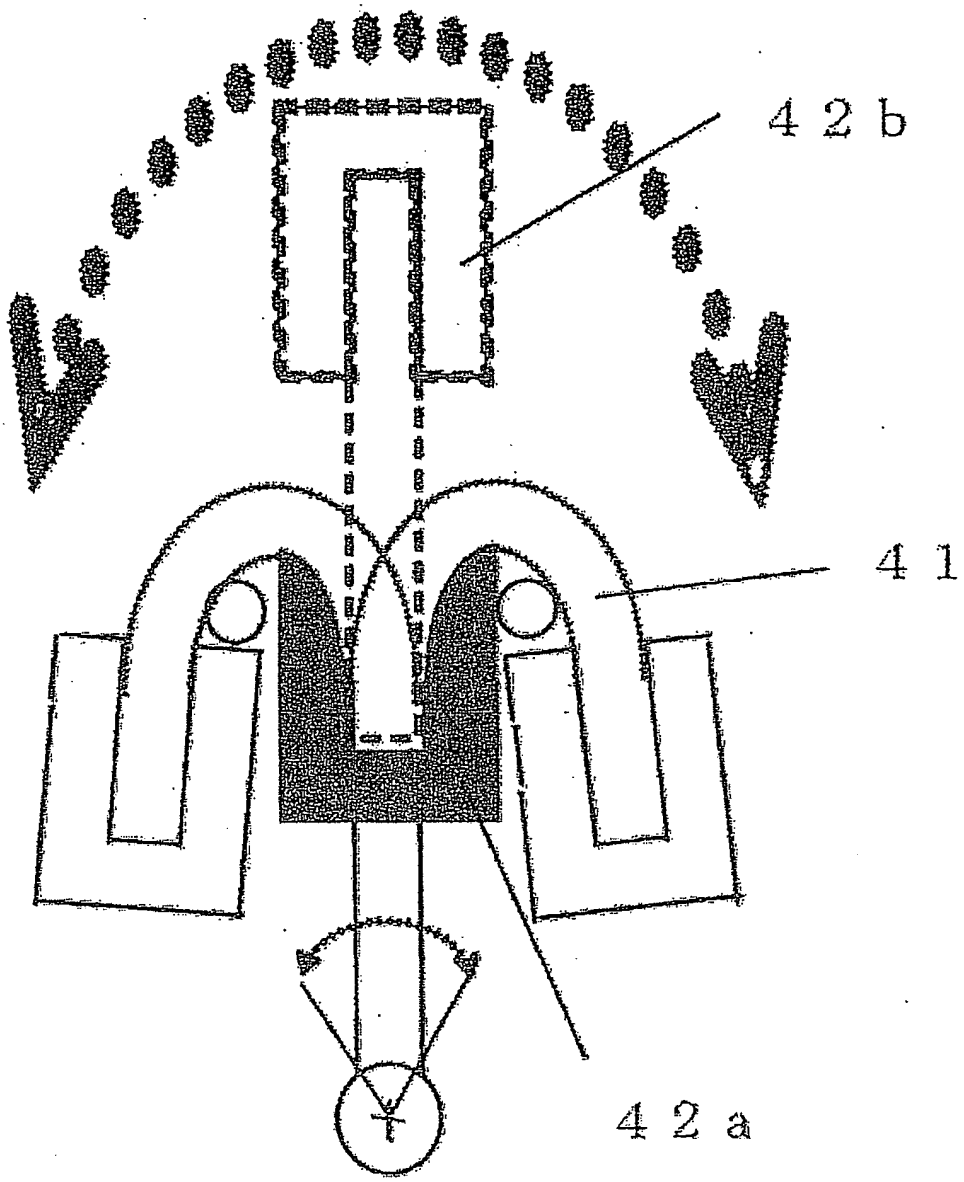

FIG. 5

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 13 00 0526

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 2 284 314 A1 (ICHIKAWA CO LTD [JP]) 16 February 2011 (2011-02-16) * the whole document * -----	1-9	INV. D21F3/02

TECHNICAL FIELDS SEARCHED (IPC)

D21F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	4 June 2013	Beckman, Anja

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

1

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 13 00 0526

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

04-06-2013

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2284314 A1	16-02-2011	BR PI1001098 A2	21-06-2011
		CA 2695828 A1	21-01-2011
		CN 101962920 A	02-02-2011
		EP 2284314 A1	16-02-2011
		JP 4444367 B1	31-03-2010
		JP 2011026711 A	10-02-2011
		KR 100972547 B1	28-07-2010
		US 2011017419 A1	27-01-2011

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2012020044 A **[0001]**
- JP 11247086 A **[0005] [0009] [0027]**
- JP 3698984 B **[0006] [0007]**
- US 7374641 B **[0006] [0007] [0027]**
- EP 0855414 A **[0006] [0007] [0027]**
- JP 3803106 B **[0006] [0007]**
- US 7090747 B **[0006] [0007]**
- JP 7292237 A **[0007]**
- JP 10212333 A **[0008]**

Non-patent literature cited in the description

- ETHACURE 300: New Curing Agent as Substitute for MOCA. *Polyfile,* January 1999, 37-38 **[0007]**
- The effect of curative on the fracture toughness of PTMEG/TDI polyurethane elastomers. *POLYMER,* 1995, vol. 36, 767-774 **[0007] [0009]**