I, Chan Wook Doh, am fluent in English and Korean. I hereby certify under penalty of perjury that I translated into English the following document: Korean Patent Application No. WO 2009/134063 A2, published on November 5, 2009, which is attached to this Affidavit. I further certify and verify under penalty of perjury that the attached document written in English is, to the best of my knowledge, a true and accurate English translation of Korean Patent Application No. WO 2009/134063 A2, published on November 5, 2009, which is written in Korean.

_____ (Signature of Translator/Verifier)

Chan Wook Doh (Print Name)

(12) International application published under the Patent Cooperation Treaty

(19) International Bureau of World Intellectual Property Organization

(43) International Publication Date
November 5, 2009 (11/05/2009)

PCT

(10) International Publication Number
WO 2009/134063 A2

(51) Classification of International Patents:
D02G 3/48 (JANUARY 2006)*D01F 6/60* (JANUARY 2006)

(21) International Application Number: PCT/KR2009/002232

(22) International Application Date: April 28, 2009 (04/28/2009)

(25) Application Language: Korean

(26) Publication Language: Korean

(30) Priority Information:
10-2008-0039924 April 29, 2008 (04/29/2008) KR
10-2008-0039993 April 29, 2008 (04/29/2008) KR
10-2008-0040179 April 30, 2008 (04/30/2008) KR

(71) Applicant (for all designated states other than the U.S.): **KOLON INDUSTRIES, INC.** [KR/KR]; 1-23 Byeoryang-dong, Gwacheon-si, Gyeonggi-do 427-040 (Kolon Tower)

(72) Inventor; and

(75) Inventor/Applicant (U.S. only): **So Yeon Kwon (KWON, So Yeon)** [KR/KR]; 874-2 Mandeok 2(i)-dong, Buk-gu, Busan 616-831 (KR).

(74) Agent: **ASTRAN INT'L IP GROUP;** 5F, 732-27 Yeoksam-dong, Gangnam-gu, Seoul 135-514 (KR) (Shinsung Building).

(81) Designated States (for the protection of all possible types of domestic rights, unless otherwise indicated): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

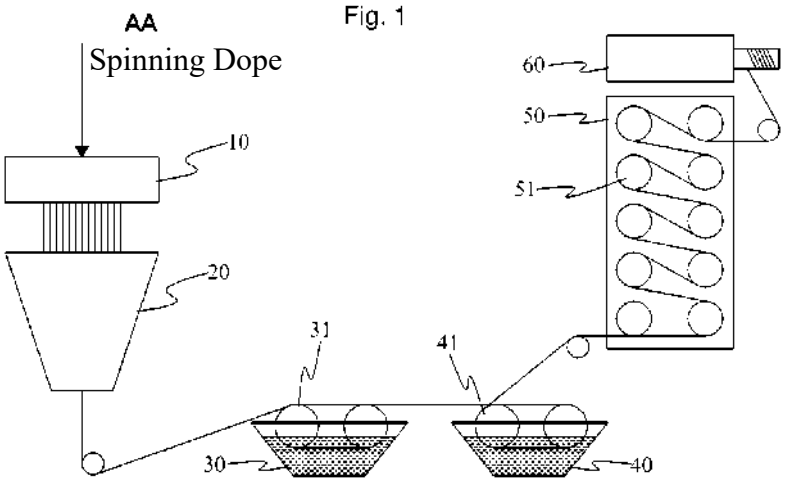
(84) Designated States (for the protection of all possible types of local rights, unless otherwise indicated): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasia (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), 유 럽 (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continue on the next page]

(54) Title: ARAMID TIRE CORD AND MANUFACTURING METHOD THEREOF

(54) Name of Invention: Aramid tire code and manufacturing method thereof

Fig. 1



AA ... spinning dope

(57) Abstract: The present invention relates to an aramid tire cord with a superior initial modulus change rate, a tensile strain and an initial modulus, and a manufacturing method thereof. The present invention provides an aramid tire cord containing an aramid multi-filament, wherein the initial modulus change rate after repetitive stretch tests performed at 10 times the load of 10% of the cutting strength at 120℃, is 5% or lower, and a manufacturing method thereof. The aramid tire cord of the present invention exhibits an excellent initial modulus change rate, a tensile strain and an initial modulus retention at a high temperature, and thus has an excellent fatigue resistance as the aramid tire cord has an optimum modulus and a crystallization constant value and a crystallization orientation constant. Accordingly, the aramid tire cord of the present invention prevents degradation of physical properties and improves travel performance even under high speed travel for long durations with a high temperature and high pressure conditions, when the aramid tire cord is used as a reinforcement material for a tire.

(57) Summary:

[Continue on the next page]

WO 2009/134063 A2

Disclosure:
— Disclosed without an international investigation report, and
separately disclosed after receipt of the report (Rule 48.2(g))

The present invention relates to an aramid tire cord having excellent initial modulus change rate, elongation strain rate and initial modulus, and a method for manufacturing the same. The present invention provides an aramid tire cord including an aramid multifilament, characterized in that the initial modulus change rate is 5% or less after 10 tensile repetition tests under a load corresponding to 10% of the breaking strength at 120°C, and a method for manufacturing the same. The aramid tire cord according to the present invention has an optimal modulus, crystallization constant value, and crystal orientation constant, and thus exhibits excellent initial modulus change rate, elongation strain rate, and initial modulus retention rate at high temperatures, and thus has excellent fatigue resistance. Therefore, when the aramid tire cord of the present invention is used as a reinforcing material for a tire, it prevents deterioration of physical properties even during high-speed driving where high temperature and high pressure conditions persist for a long time, thereby exhibiting excellent driving performance.

Specifications

Aramid Tire Codes and Manufacturing Method Thereof

Technical Field

[1] The present invention relates to an aramid tire cord and a method for manufacturing the same, and more specifically, to an aramid tire cord having excellent initial modulus, elongation strain rate, initial modulus and breaking strength retention, and thereby minimizing deterioration of physical properties even during long-time high-speed driving when used as a tire reinforcing material, and a method for manufacturing the same.

Background Technology

[2] Tire cord, especially tire cord treated with adhesive, is widely used as a reinforcing material for rubber products such as tires. Materials for tire cords include nylon fibers, polyester fibers, and cellulose-based regenerated fibers. One of the important ways to improve the performance of final rubber products is to improve the physical properties of the tire cord used as a reinforcing material.

[3] Nylon fibers, which generally have excellent elongation and breaking strength, are used as reinforcing materials in tires of large trucks subjected to high loads and vehicles that run on bumpy roads such as unpaved roads. However, because nylon fibers have a low modulus, they are not suitable for tires for racing cars that drive at high speeds or for passenger cars that require good ride comfort.

[4] Polyester fibers are continuously increasing in use in the tire cord field due to their superior dimensional stability and price competitiveness compared to nylon fibers, but they are not suitable for tires for high-speed vehicles due to their low heat resistance and low adhesive strength with rubber.

[5] Regenerated cellulose fibers, such as rayon fibers, exhibit excellent breaking strength retention and dimensional stability at high temperatures. However, regenerated cellulose fibers have a severe decrease in breaking strength due to moisture, so thorough moisture management is required during tire manufacturing, and above all, there is the problem that the breaking strength is too low for the price, compared to other materials.

[6] Meanwhile, tire reinforcing fiber cords used in heavy equipment vehicles, racing vehicles, aircraft, agricultural vehicles, etc. are required to have strength and modulus much higher than those obtainable by polyester fibers or nylon fibers.

[7] Fibers that can provide such high strength and modulus are so-called aramid fibers, a type of aromatic polyamide fiber.

[8] However, since aramid fibers have inherently high modulus and low elongation characteristics, tire cords manufactured using them generally have the following problems due to low fatigue resistance when subjected to repeated tensile fatigue under conditions of high load and high stress.

[9] Normally, when a car is driven, the temperature of the tire rises due to friction, and as high temperature and high pressure conditions are maintained for a long time, especially during high-speed driving, the tire reinforcing fiber cord is also exposed to high temperature and high pressure fatigue conditions. At this time, if the fatigue resistance of the fiber cord is low, the physical properties of the cord, especially the breaking strength, may rapidly deteriorate due to repeated tension and contraction, which may significantly deteriorate the driving performance of the tire. In severe cases, the tires may also rupture while driving.

Detailed Description of Invention

Technical Challenges

[10] The present invention has been made to solve the above problems, and aims to manufacture an aramid tire cord capable of exhibiting excellent driving performance by having low property degradation even when driving at high speeds with high temperature and high pressure conditions repeated for a long period of time.

Technical Solutions

[11] In order to achieve the above object, the present invention provides an aramid tire cord including an aramid multifilament, characterized in that the initial modulus change rate is 5% or less after 10 tensile repetition tests under a load corresponding to 10% of the breaking strength at 120°C, as defined by Calculation Formula 1 below.

[12] [Calculation Formula 1]

[13] Initial modulus change rate (%) = [(M1 - M2) / M1 × 100

[14] (In the above formula, M1 is the initial modulus (g/d) value before the tensile repetition test, and M2 is the initial modulus (g/d) value after the tensile repetition test.)

[15] Meanwhile, the aramid tire cord can have an initial modulus change rate of 5% or less after 10 tensile repetition tests under a load corresponding to 10% of the breaking strength at 150°C, as defined by Calculation Formula 1 above.

[16] In addition, the aramid tire cord can have a strength retention rate of 95% or more after 10 tensile repetition tests under a load corresponding to 10% of the breaking strength at 120°C, as defined by Calculation Formula 2 below.

[17] [Calculation Formula 2]

[18] Strength retention rate (%) = (S2 / S1) × 100

[19] (In the above formula, S1 is the strength (g/d) value before the tensile repetition test, and S2 is the strength (g/d) value after the tensile repetition test.)

[20] Meanwhile, the aramid tire cord can have a strength retention rate of 90% or more after 10 tensile repetition tests under a load corresponding to 10% of the breaking strength at 150°C, as defined by Calculation Formula 2 above.

[21] In addition, the aramid tire cord can have an elongation strain rate of 0.01 to 0.3% after being left for 100 hours under a load corresponding to 20% of the breaking strength at 30°C, as defined by Calculation Formula 3 below.

[22] [Calculation Formula 3]

[23] Elongation strain rate (%) = [(L1 - L0) / L0] × 100

[24] (In the above formula, L0 represents the length value of the aramid tire cord before applying a load, and L1 represents the length value of the aramid tire cord after being left for 100 hours under a load corresponding to 20% of the breaking strength of the aramid tire cord at 30℃.)

[25] Meanwhile, the aramid tire cord can have an elongation strain rate of 0.3 to 1.0% after being left for 100 hours under a load corresponding to 20% of the breaking strength at 120°C, as defined by Calculation Formula 3 above.

[26] In addition, it is preferable that the aramid tire cord have an initial modulus retention rate of 95% or more, as defined by Calculation Formula 4 below.

[27] [Calculation Formula 4]

[28] Initial modulus retention rate (%) = (M'2 / M'1) × 100

[29] (In the above formula, M'1 is the initial modulus (g/d) value of the aramid tire cord measured after leaving it at 25℃, 65RH% for 100 hours, and M'2 is the initial modulus (g/d) value of the aramid tire cord measured after leaving it at 80℃, 80RH% for 100 hours.)

[30] In addition, it is desirable that the aramid tire cord have a breaking strength retention of 95% or higher, as defined by Calculation Formula 5 below.

[31] [Calculation Formula 5]

[32] Breaking Strength Retention (%) = (S'2 / S'1) × 100

[33] (In the above formula, S'1 is the breaking strength (g) value of the aramid tire cord measured after leaving it at 25℃, 65RH% for 100 hours, and S'2 is the breaking strength (g) value of the aramid tire cord measured after leaving it at 80℃, 80RH% for 100 hours.)

[34] In addition, it is preferable that the aramid multifilament has a crystallization constant value of 0.9 to 1.0, as defined by Calculation Formula 6 below.

[35] [Calculation Formula 6]

[36] Crystallization constant = C × D

[37] (In the above formula, C is the crystallinity of the aramid multifilament, and D is the density of the aramid multifilament (g/cm3).)

[38] Meanwhile, aramid multifilament is defined by Calculation Formula 7 below and preferably has a crystal orientation constant of 0.5 to 0.7.

[39] [Calculation Formula 7]

[40] Crystal orientation constant = Xc × Fc

[41] (In the above formula, Xc is the crystallinity value of the aramid multifilament, and Fc is the orientation value of the aramid multifilament.)

[42] In addition, it is desirable for the aramid multifilament to have a modulus of 400 to 750 g/d.

[43] Meanwhile, the aramid multifilament may include poly(para-phenylene terephthalamide).

[44] In addition, it is desirable for the aramid tire cord to have an intermediate elongation of 0.3 to 1.5% under a load of 6.75 kg.

[45] In addition, it is desirable for the aramid tire cord to have a dry heat shrinkage rate of 0.3 to -1.0%.

[46] In another aspect of the present invention, a method for manufacturing an aramid tire cord is provided, comprising the steps of: spinning a spinning dope comprising an aromatic polyamide polymer; coagulating the spun material to form a multifilament; washing the multifilament; and drying and winding the washed multifilament,

[47] wherein the step of coagulating the spinning dope comprises a process of coagulating after passing the spinning dope through holes in a spinneret, and then sequentially passing it through an air gap, a coagulation bath containing a coagulating solution including sulfuric acid having a sulfuric acid concentration of 3% or less, and a coagulation tube, and wherein a shear rate (SR) in the spinneret and a stretch factor (SF) in the air gap satisfy Calculation Formula 8 below.

[48] [Calculation Equation 8]

[49] $50{,}000 \leq SR + (20{,}000 \times SF) \leq 1{,}000{,}000$

[50] (Here, the shear rate (SR) (sec-1) is the value obtained by dividing the speed (m/min) of the spinning dope passing through the hole of the spinneret by the diameter (μm) of the hole of the spinneret, and the stretch factor (SF) is the speed (m/min) of the filament emitted from the coagulation tube/the speed (m/min) of the spinning dope emitted from the hole of the spinneret.)

[51] At this time, it is preferable that the distance from the top of the coagulation solution stored in the coagulation bath to the nozzle provided in the coagulation tube is in the range of 10 to 35 mm.

[52] Meanwhile, in the above-mentioned winding step, it is preferable to wind the dried multifilament at 700 to 1,500 m/min.

[53] In addition, the method may include a step of manufacturing an aramid cabled yarn from the manufactured aramid multifilament; a step of immersing the aramid cabled yarn in an adhesive resin solution containing resorcinol-formaldehyde-latex (RFL); a step of drying the immersed aramid cabled yarn at 105 to 200°C for 10 to 400 seconds; and a step of heat-treating the dried aramid cabled yarn at 105 to 300°C for 10 to 400 seconds, thereby manufacturing an aramid tire cord.

Beneficial Effects

[54] The aramid tire cord according to the present invention has an optimal modulus, crystallization constant value, and crystal orientation constant, and thus exhibits excellent initial modulus change rate, elongation strain rate, and initial modulus retention rate at high temperatures, and thus has excellent fatigue resistance. Therefore, when the aramid tire cord of the present invention is used as a reinforcing material for a tire, it prevents deterioration of physical properties even during high-speed driving with high temperature and high pressure conditions repeated for a long period of time, thereby exhibiting excellent driving performance.

Brief Description of the Drawings

[55] FIG. 1 schematically illustrates a process for manufacturing an aramid multifilament according to one embodiment of the present invention.

[56] Figure 2 is a schematic diagram of a spinning device according to one embodiment of the present invention.

[57] <Explanation of symbols for Major Parts of the Drawings>

[58] 1: multifilament 10: spinneret

[59] 15: hole of spinneret 17: air gap

[60] 20: coagulation section 21: coagulation bath

[61] 22: coagulation solution 23: coagulation tube

[62] 24: nozzle

[63] 30: 1st washing tank 31: 1st washing roll

[64] 40: 2nd washing tank 41: 2nd washing roll

[65] 50: drying section 51: drying roll

[66] 60: winder

[67]

Form for Carrying Out the Invention

[68] Hereinafter, one embodiment of a method for manufacturing an aramid tire cord of the present invention will be specifically described with reference to the accompanying drawings.

[69] First, the aramid multifilament for manufacturing the aramid tire cord of the present invention can be manufactured using an aromatic polyamide polymer manufactured by the following method:

[70] Aromatic polyamide polymers can be prepared as follows:

[71] A polymerization solvent is prepared by adding an inorganic salt to an organic solvent. The organic solvent may be an amide-based organic solvent, a urea-based organic solvent, or a mixed organic solvent thereof. Specific examples thereof include N-methyl-2-pyrrolidone (NMP), N, N'-dimethylacetamide (DMAc), hexamethylphosphoramide (HMPA), N, N, N', N'-tetramethyl urea (TMU), N, N-dimethylformamide (DMF), or a mixture thereof.

[72] Next, an aromatic diamine is dissolved in the polymerization solvent prepared above to prepare a mixed solution. Specific examples of aromatic diamines include, but are not limited to, para-phenylenediamine, 4,4'-diaminobiphenyl, 2,6-naphthalenediamine, 1,5-naphthalenediamine or 4,4'-diaminobenzanilide.

[73] Next, while stirring the mixed solution, a small, predetermined amount of aromatic diacid halide is added to the mixed solution to perform prepolymerization. Specific examples of aromatic diacid halides include, but are not limited to, terephthaloyl dichloride, 4,4'-benzoyl dichloride, 2,6-naphthalenedicarboxylic acid dichloride or 1,5-naphthalenedicarboxylic acid dichloride.

[74] After completing the prepolymerization process, an aromatic diacid halide is additionally added to the prepolymer to produce a final polymer.

[75] Specific examples of aromatic polyamide polymers obtained by the polymerization process include poly(paraphenylene terephthalamide: PPD-T), poly(4,4'-benzanilide terephthalamide), poly(paraphenylene-4,4'-biphenylene-dicarboxylic acid amide), or poly(paraphenylene-2,6-naphthalenedicarboxylic acid amide).

[76] Next, the acid generated during the polymerization reaction is neutralized and removed using an alkaline compound, and then the acid is pulverized and the polymerization solvent is extracted.

[77] Next, the water remaining after the extraction process is dehydrated, and then a drying process is performed to complete the production of an aromatic polyamide polymer.

[78] An aromatic polyamide polymer having an intrinsic viscosity of 5.0 or higher, manufactured as described above, is dissolved in a concentrated sulfuric acid solvent having a concentration of 97 to 100% to manufacture a spinning dope. Instead of the above sulfuric acid, chlorosulfuric acid or fluorosulfuric acid can also be used. Meanwhile, in order to perform a smooth spinning process, it is preferable that the spinning dope have a polymer concentration of 10 to 25 wt%.

[79] Next, using the aromatic polyamide polymer manufactured by the above method, an aramid multifilament is manufactured as shown in Fig. 1.

[80] A spinning dope prepared by dissolving an aromatic polyamide polymer having an intrinsic viscosity (IV) of 5.0 to 7.0, for example, poly para-phenylene terephthalamide (PPD-T), in a concentrated sulfuric acid solvent is spun using a spinneret (10), and then coagulated in a coagulation bath (20) through an air gap, which is a non-coagulated fluid layer, to form a multifilament.

[81] Next, the sulfuric acid remaining in the multifilament obtained is removed. The sulfuric acid remaining in the multifilament is removed by passing it through a washing tank (30, 40) containing water or a mixed solution containing water and an alkaline solution.

[82] Next, a drying process to remove moisture remaining in the multifilament is performed in a drying roll (50), and the dried multifilament is wound in a winder (60) to finally manufacture an aramid multifilament.

[83] Meanwhile, since aramid multifilament used in tire cords typically has a high modulus and degree of crystallinity, aramid tire cords manufactured from it typically have the following problems due to low fatigue resistance when subjected to repeated tensile fatigue under conditions of high load and high stress.

[84] Such aramid cord for reinforcing tires with low fatigue resistance has its properties deteriorated during high-speed driving with repeated high temperatures and pressures, resulting in a significant deterioration in driving performance.

[85] Accordingly, the present invention aims to provide an aramid multifilament having an optimal modulus, crystallization constant value, and crystal orientation constant for manufacturing an aramid tire cord having excellent initial modulus change rate, elongation strain rate, and initial modulus retention rate, thereby improving the fatigue resistance of the tire cord.

[86] As a method for achieving this, the present invention aimed to manufacture an aramid multifilament having an optimal modulus, crystallization constant value, and crystal orientation constant by spinning and coagulating a spinning dope under appropriate spinning and coagulation conditions.

[87] Under these spinning conditions, the inventors of the present invention have found through numerous tests that the crystal structure of aramid multifilament is greatly affected by the shear rate and stretch factor. Meanwhile, in the case of coagulation conditions, the inventors of the present invention have also found through numerous tests that the crystal structure of aramid multifilament is greatly affected by the composition of the coagulation solution (22) and the structure of the coagulation section (22).

[88] First, the present invention will be described with reference to Fig. 2, which schematically illustrates a spinning device, to explain optimal spinning and coagulation conditions. As can be seen in Fig. 2, the multifilament is formed by passing the spinning dope through the hole (15) of the spinneret and then through the air gap (17), coagulation bath (21), and coagulation tube (23) in sequence to coagulate it.

[89] The spinneret (10) has a plurality of spinneret holes (15) of a predetermined diameter (R). It is preferable that the diameter of the hole (15) of the above-mentioned spinneret is 0.1 mm or less. If the diameter of the hole (15) of the above-mentioned spinneret exceeds 0.1 mm, the molecular orientation of the filament produced may deteriorate, which may result in a decrease in the strength of the filament.

[90] The above coagulation bath (21) is located at the bottom of the above-mentioned spinneret (10) and a coagulation solution is stored inside it, and a coagulation tube (23) is formed at the bottom of the above-mentioned coagulation bath (21). Accordingly, the spun material passing through the hole (15) of the above-mentioned spinneret is coagulated to form a filament while passing through the air gap (17) and the coagulating solution (22) sequentially as it descends, and this filament is discharged while passing through the coagulating tube (23) at the bottom of the coagulating bath (21). Since the coagulation solution is discharged through the coagulation tube along with the filament, the coagulation solution (22) must be continuously supplied to the coagulation bath (21) in the amount of the discharged solution. In addition, a nozzle (24) is formed in the coagulation tube (23) so that a coagulation solution can be sprayed onto a filament passing through the coagulation tube (23).

[91] Meanwhile, in order to manufacture an aramid multifilament having an optimal modulus, crystallization constant value, and crystal orientation constant, the shear rate (SR) within the spinneret (10) and the stretch factor (SF) in the single air gap satisfy Calculation Formula 8.

[92] [Calculation Formula 8]

[93] $50{,}000 \leq SR + (20{,}000 \times SF) \leq 1{,}000{,}000$

[94] In Calculation Formula 8 above, the shear rate (SR) (sec-1) is a value obtained by dividing the speed (m/min) of the spinning dope passing through the hole (15) of the spinneret by the diameter (R) (μm) of the hole of the spinneret, and the stretch factor (SF) is a value obtained by dividing the speed (m/min) of the filament emitted from the coagulation tube (23) by the speed (m/min) of the spinning dope emitted from the hole (15)

of the spinneret.

[95] In order to satisfy such conditions, when the speed of the spinning dope passing through the hole (15) of the spinneret, the diameter (R) of the hole of the spinneret, the speed of the filaments emitted from the coagulation tube (30), and the speed of the spinning dope emitted from the hole (15) of the spinneret are appropriately set, the aramid multifilament obtained has a modulus of 400 to 750 g/d.

[96] When the value of the above SR + (20,000 × SF) becomes less than 50,000, the degree of orientation of the aramid multifilament decreases and the modulus becomes less than 400 g/d, and when the value of the above SR+(20,000×SF) becomes greater than 1,000,000, the modulus of the aramid multifilament becomes greater than 750 g/d, but defects increase and the optimal crystal constant value and crystal orientation constant described later cannot be obtained. Tire cords manufactured using aramid multifilament manufactured in this manner have low fatigue resistance, and therefore, when driven at high speeds for long periods of time under high temperature and high pressure conditions, the driving performance is significantly reduced due to rapid deterioration of physical properties.

[97] Next, it is preferable that the distance (L) from the top of the coagulation solution (22) stored in the coagulation bath (21) to the nozzle (24) provided in the coagulation tube (23), more precisely to the top of the nozzle (24), be in the range of 10 to 35 mm. If the above distance (L) is less than 10 mm, there is a risk that the crystal orientation of the filament may be damaged because the coagulation solution may be sprayed while the filament is not sufficiently coagulated, and if the above distance (L) exceeds 35 mm, there is a risk that the surface of the filament may be damaged because the coagulation solution may be sprayed while the filament is completely coagulated. In this way, the process of spraying the coagulation solution from the nozzle (24) must be performed in a state where the filament is appropriately coagulated, and considering this, the distance (L) is set to a range of 10 to 35 mm.

[98] The distance (L1) from the top of the coagulation solution (22) to the bottom of the coagulation bath (21) should, preferably, be in the range of 5 to 15 mm. If the above distance (L1) is less than 5 mm, eddies caused by air may occur, making it difficult to control the spinning process. If the above distance (L1) exceeds 15 mm, too much coagulation of the filament may occur within the coagulation bath (21), making it difficult to set the formation position of the nozzle (24). In other words, when a large amount of filament coagulation occurs within the coagulation bath (21), there is a burden of having to set the position of the nozzle (24) close to the top of the coagulation tube (23) so that the coagulation solution can be sprayed before the filament is completely coagulated. In addition, if the nozzle (24) is set too close to the top of the coagulation tube (23), a problem may occur in which the spraying is performed in a state where the filament is not focused sufficiently.

[99] The distance (L2) from the bottom of the above coagulation bath (21) to the nozzle (24), more precisely to the top of the nozzle (24) should, preferably, be in the range of 5 to 20 mm. If the above distance (L2) is less than 5 mm, the spraying is performed while the filament is not focused sufficiently, so uniform coagulation of the filament may not occur, and if the above distance (L2) exceeds 20 mm, the pumping capacity for the coagulation

solution (22) stored in the coagulation bath (21) may be reduced. In other words, when the coagulation solution is sprayed from the nozzle (24), a pressure difference occurs between the coagulation bath (21) and the coagulation tube (23), so that the coagulation solution stored in the coagulation bath (21) is pumped to move quickly into the coagulation tube (23). However, if the nozzle (24) is formed at a location too far from the bottom of the coagulation bath (21), the pumping capacity for such coagulant is reduced.

[100] Next, the coagulation solution of the present invention should, most preferably, be an aqueous solution containing sulfuric acid with a sulfuric acid concentration of 3% or less. The concentration of sulfuric acid in an aqueous solution has a significant effect on the crystal structure, such as crystal size and crystallinity.

[101] If the coagulation solution does not contain sulfuric acid, the large sulfuric acid concentration gradient causes sulfuric acid to rapidly escape from the spinning dope, resulting in a large difference in the crystal structure between the inner and outer layers of the multifilament. This results in a rapid release of sulfuric acid in the outer layer, preventing the formation of stable crystals, resulting in a small crystal size and low crystallinity. On the other hand, in the inner layer, sulfuric acid is slowly released, causing the crystal size to increase and the degree of crystallinity to increase. Such multifilaments, which have large differences in properties between the inner and outer layers, have extremely low modulus and breaking strength, and when they are used in tire cords, the properties deteriorate rapidly at high temperatures and at high speeds, causing serious problems in driving stability.

[102] Meanwhile, when the sulfuric acid concentration of the coagulation solution exceeds 3%, the sulfuric acid slowly escapes from the spinning dope due to the low sulfuric acid concentration gradient, so that the structures of the inner and outer layers of the multifilament do not show a significant difference. Thus, the multifilament formed has a large crystal size and high crystallinity, resulting in an excessively high modulus, etc. However, tire cords manufactured using aramid multifilament having a high modulus have poor initial modulus change rate, elongation strain rate, and initial modulus retention rate, resulting in low fatigue resistance, and when driving at high speeds for long periods of time under high temperature and high pressure conditions, the physical properties rapidly deteriorate, significantly reducing driving performance. Also, in severe cases, the risk of tire rupture while driving increases.

[103] Therefore, in order to manufacture an aramid multifilament having an optimal modulus and crystal structure, a coagulation solution containing sulfuric acid with a sulfuric acid concentration of 3% or less should, preferably, be used to coagulate the spun yarn.

[104] In addition, it was found that an appropriate winding speed is necessary to manufacture an aramid multifilament having the optimal crystallization constant value and crystal orientation constant of the present invention. The winding speed has a great influence on the crystal orientation of aramid multifilament. As the winding speed increases, the shear stress gradually increases, which increases the crystal orientation and thus the modulus.

[105] However, if the winding speed is too high, excessive shear stress is formed, which creates a large number of non-uniform crystals and reduces the breaking strength. Aramid multifilament manufactured in this way has low breaking strength and high modulus, and

tire cords manufactured using this have low fatigue resistance, which significantly reduces driving performance due to rapid deterioration of physical properties when driving at high speeds for long periods of time under high temperature and high pressure conditions.

[106] On the other hand, if the winding speed is excessively low, the shear stress becomes too small, making it impossible to obtain high orientation crystals and reducing productivity. In addition, since it has a small modulus due to low orientation crystals, when used as a reinforcing material for tire cord, the dimensional stability is reduced during high-speed driving under high temperature and high pressure conditions, resulting in poor driving performance.

[107] Therefore, the present invention should, preferably, manufacture aramid multifilament at a winding speed of 700 to 1,500 m/min. If the winding speed is less than 700 m/min, productivity decreases and durability and dimensional stability are deteriorated due to low modulus. On the other hand, when the winding speed exceeds 1,500 m/min, the orientation crystals increase, forming a high modulus and low breaking strength, which lowers the physical properties during high-speed driving due to low fatigue resistance and durability, thereby reducing driving performance.

[108] The aramid multifilament manufactured according to the present invention has a crystallization constant value of 0.9 to 1.0, as defined by Calculation Formula 6 below.

[109] [Calculation Formula 6]

[110] Crystallization constant value = C × D

[111] (In the above formula, C is the crystallinity of the aramid multifilament, and D is the density of the aramid multifilament (g/cm2))

[112] If the crystallization constant value of the aramid multifilament exceeds 1.0, the aramid tire cord manufactured from it has a high modulus due to the high crystallinity, which reduces driving performance and tire moldability due to low fatigue resistance. On the other hand, when the crystallization constant value of the aramid multifilament is less than 0.9, it does not have sufficient breaking strength and modulus due to the low crystallinity, and the aramid tire cord manufactured from it has poor durability and dimensional stability due to the high initial modulus change rate and low strength retention rate.

[113] In addition, the aramid multifilament manufactured according to the present invention has a crystal orientation constant of 0.5 to 0.7, as defined by Calculation Formula 7 below.

[114] [Calculation Formula 7]

[115] Crystal orientation constant = Xc × Fc

[116] (In the above formula, Xc is the crystallinity value of the aramid multifilament, and Fc is the orientation value of the aramid multifilament.)

[117] If the crystal orientation constant of the aramid multifilament exceeds 0.7, the aramid tire cord manufactured from this has low fatigue resistance due to excessive modulus caused by high crystal orientation, thereby reducing driving performance. It also reduces tire moldability. On the other hand, when the crystal orientation constant of the aramid multifilament is less than 0.5, it does not have sufficient modulus and breaking strength due to low crystal orientation, and therefore, the aramid tire cord manufactured from it

has poor initial modulus change rate and strength retention rate under high temperature and high humidity conditions, and thus has poor dimensional stability and durability during high-speed driving.

[118] In addition, the aramid multifilament manufactured according to the present invention has a modulus of 400 to 750 g/d. If the modulus of the aramid multifilament exceeds 750 g/d, the aramid tire cord manufactured from it has low fatigue resistance due to the excessive modulus, resulting in poor driving performance and reduced tire moldability. On the other hand, when the modulus of the aramid multifilament is less than 400 g/d, the aramid tire cord manufactured from it has insufficient support capability for high-speed driving due to poor resistance to sufficient external force caused by the low modulus, thereby reducing driving performance.

[119] Next, the process for manufacturing aramid tire cord is described.

[120] First, aramid multifilaments are z-twisted and s-twisted to produce a cabled yarn to improve breaking strength and increase adhesion to rubber.

[121] Aramid multifilament is z-twisted using a spinning machine, then combined and s-twisted to produce a cabled yarn. Meanwhile, in the present invention, it is preferable that the twist count of the z- and s-twists be 20 to 60 times/10 cm each. If the above-mentioned twist count is less than 20 times/10 cm, the breaking strength of the cabled yarn is high, but the elongation at break is low, which reduces the fatigue resistance of the tire cord. In addition, the surface area of the cabled yarn is reduced, which reduces its adhesion to the rubber. On the other hand, if the above-mentioned twist count exceeds 60 times/10 cm, the strength of the tire cord is excessively reduced.

[122] The cabled yarn manufactured in this way is immersed in an adhesive resin solution containing resorcinol-formaldehyde-latex (RFL). At this time, either one-bath dipping or two-bath dipping can be used.

[123] Meanwhile, the present invention can weave using the cabled yarn and treat the woven cord paper with adhesive resin before directly treating the cabled yarn with adhesive resin.

[124] According to one embodiment of the present invention, the cabled yarn is immersed so that the pickup rate of the adhesive resin is 3 to 12 wt% based on the cabled yarn. When the pickup rate is less than 3 wt%, the adhesive strength of the aramid tire cord to rubber is reduced, and when the pickup rate exceeds 12 wt%, the adhesive resin excessively penetrates into the cabled yarn, reducing the breaking strength and fatigue resistance.

[125] The aramid tire cord is completed by drying the cabled yarn containing the adhesive resin solution by immersion at 105 to 200°C for 10 to 400 seconds and then heat-treating it at 105 to 300°C for 10 to 400 seconds. The drying process is to remove moisture present in the cabled yarn, and the heat treatment process is to improve the adhesion between the aramid tire cord and rubber by reacting the adhesive resin solution contained in the cabled yarn.

[126] Meanwhile, if the drying and heat treatment times are each shorter than the above ranges, or if the drying and heat treatment temperatures are each lower than the above ranges, the adhesive strength between the aramid tire cord and rubber decreases.

[127] Conversely, if the drying and heat treatment times are longer than the above ranges, or if the drying and heat treatment temperatures are higher than the above ranges, not only will

the adhesive strength between the aramid tire cord and rubber decrease, but also the physical properties such as breaking strength and fatigue resistance will deteriorate.

[128] The aramid tire cord manufactured in this manner is defined by Calculation Formula 1 below and has an initial modulus change rate of 5% or less after 10 tensile repetition tests under a load corresponding to 10% of the breaking strength at 120°C.

[129] [Calculation Formula 1]

[130] Initial modulus change rate (%) = [(M1 - M2) / M1 × 100

[131] (In the above formula, M1 is the initial modulus (g/d) value before the tensile repetition test, and M2 is the initial modulus (g/d) value after the tensile repetition test.)

[132] Meanwhile, the aramid tire cord is defined by Calculation Formula 1 above and is characterized by an initial modulus change rate of 5% or less after 10 tensile repetition tests under a load corresponding to 10% of the breaking strength at 150°C.

[133] If the initial modulus change rate of the aramid tire cord exceeds 5%, the dimensional stability is reduced under repeated tensile conditions during high-speed driving, thereby deteriorating driving performance.

[134] In addition, the aramid tire cord manufactured in this manner is characterized by having a strength retention rate of 95% or more after 10 tensile repetition tests under a load corresponding to 10% of the breaking strength at 120°C, as defined by Calculation Formula 2 below.

[135] [Calculation Formula 2]

[136] Strength retention rate (%) = (S2 / S1) × 100

[137] (In the above formula, S1 is the strength (g/d) value before the tensile repetition test, and S2 is the strength (g/d) value after the tensile repetition test.)

[138] Meanwhile, the aramid tire cord is defined by Calculation Formula 2 above and is characterized by having a strength retention rate of 90% or more after 10 tensile repetition tests under a load corresponding to 10% of the breaking strength at 150°C.

[139] If the strength retention rate of the aramid tire cord does not meet the above range, the ability to support the tire is reduced due to deterioration of physical properties during driving, resulting in deterioration of driving performance and, in severe cases, tire rupture.

[140] In addition, the aramid tire cord manufactured in this manner is characterized by having an elongation strain rate of 0.01 to 0.3% after being left for 100 hours under a load corresponding to 20% of the breaking strength at 30°C, as defined by Calculation Formula 3 below.

[141] [Calculation Formula 3]

[142] Elongation strain rate (%) = [(L1 - L0) /L0] × 100

[143] (In the above formula, L0 represents the length value of the aramid tire cord before applying a load, and L1 represents the length value of the aramid tire cord after being left for 100 hours under a load corresponding to 20% of the breaking strength of the aramid tire cord at 30°C or 120°C.)

[144] Meanwhile, the aramid tire cord is characterized by having an elongation strain rate of 0.3 to 1.0% after being left for 100 hours under a load corresponding to 20% of the breaking strength at 120°C, as defined by Calculation Formula 3 above.

[145] During high-speed driving, tires become hot and the shape of the tire cord changes

accordingly. Then, when driving comes to a halt, the temperature of the tire drops and the part of the tire in contact with the ground continues to receive the load of the car, so it maintains its deformed shape, while the rest of the tire is no longer under load and returns to its original shape. Accordingly, when the elongation strain rate of the aramid tire cord is high at high temperatures, a problem occurs in which the ride comfort of the vehicle is significantly reduced.

[146] If the elongation strain rate of the aramid tire cord is outside the above range, the aramid tire cord undergoes significant deformation under repeated tensile conditions, which reduces the ability to support the tire, lowers durability and dimensional stability, and significantly reduces ride comfort during driving.

[147] In addition, the aramid tire cord is characterized by having an initial modulus retention rate of 95% or more, as defined by Calculation Formula 4 below.

[148] [Calculation Formula 4]

[149] Initial modulus retention rate (%) = (M'2 / M'1) × 100

[150] (In the above formula, M'1 is the initial modulus (g/d) value of the aramid tire cord measured after leaving it at 25℃, 65RH% for 100 hours, and M'2 is the initial modulus (g/d) value of the aramid tire cord measured after leaving it at 80℃, 80RH% for 100 hours.)

[151] Meanwhile, the aramid tire cord is defined by Calculation Formula 5 below and is characterized by having a breaking strength retention of 95% or higher.

[152] [Calculation Formula 5]

[153] Breaking Strength Retention (%) = (S'2 / S'1) × 100

[154] (In the above formula, S'1 is the breaking strength (g) value of the aramid tire cord measured after leaving it at 25℃, 65RH% for 100 hours, and S'2 is the breaking strength (g) value of the aramid tire cord measured after leaving it at 80℃, 80RH% for 100 hours.)

[155] If the initial modulus change rate and strength retention rate of the aramid tire cord are outside the above range, the dimensional stability and durability are reduced during high-speed driving, thereby reducing driving performance.

[156] In addition, the aramid tire cord manufactured in this manner is characterized by having an intermediate elongation of 0.3 to 1.5% under a load of 6.75 kg.

[157] If the intermediate elongation exceeds 1.5%, a significant deformation of the cord occurs during the driving process where driving and stopping are repeated, which reduces the dimensional stability during high-speed driving and significantly reduces the ride comfort. On the other hand, when the intermediate elongation is less than 0.3%, the tire moldability is greatly reduced.

[158] Furthermore, the aramid tire cord manufactured in this manner is characterized by having a dry heat shrinkage rate of 0.3 to -1.0%.

[159] If the dry heat shrinkage rate is outside the above range, the cord shrinks significantly due to the increase in temperature inside the tire during high-speed driving, which reduces the dimensional stability of the cord and lowers the tire performance.

[160] In addition, the aramid tire cord manufactured in this way has a dip strength of 10 to 23 g/d, an elongation at break of 3 to 10%, and an adhesive strength of 10 kg or more.

[161] Hereinafter, the present invention will be specifically described through embodiments and comparative examples. However, the following embodiments are only intended to aid understanding of the present invention and should not be construed as limiting the scope of the present invention.

[162] First, aramid multi filaments were prepared according to the following method.

[163] Embodiment 1

[164] An aromatic diamine solution was prepared by maintaining 1,000 kg of N-methyl-2-pyrrolidone at 80°C and dissolving 80 kg of calcium chloride and 48.67 kg of para-phenylenediamine in it.

[165] The above aromatic diamine solution was introduced into a polymerization reactor, and at the same time, molten terephthaloyl chloride in an equimolar amount as para-phenylenediamine was introduced into the polymerization reactor, and these were stirred to produce a poly(para-phenylene terephthalamide) polymer (aramid polymer) having an intrinsic viscosity of 6.8.

[166] Next, the above-mentioned manufactured aramid polymer was dissolved in 99% concentrated sulfuric acid to prepare an optically anisotropic spinning solution having a polymer content of 18 wt%.

[167] Next, the spinning solution prepared as described above was spun at a spin winding speed of 1,000 m/min through a spinneret as shown in FIG. 2, and then the spun material was passed through an air gap of 7 mm (non-coagulable fluid layer) and then continuously passed into a coagulation section (20) containing a coagulation solution containing a sulfuric acid solution having a sulfuric acid concentration of 2.5% to form a multifilament. At this time, the shear rate (SR) within the spinneret was 10,000 and the stretch factor (SF) in the air gap was 2, so the value of SR + (20,000 × SF) was 50,000.

[168] Meanwhile, the distance (L) from the top of the coagulation solution (22) stored in the coagulation bath (21) of the coagulation section (20) to the nozzle (24) provided in the coagulation tube (23) was set to 20 mm, the distance (L1) from the top of the coagulation solution (22) to the bottom of the coagulation bath (21) was set to 10 mm, and the distance (L2) from the bottom of the coagulation bath (21) to the nozzle (24) was set to 10 mm.

[169] Next, the multifilament formed as described above was subjected to a process of washing and drying as shown in Fig. 1, and then heat-treating at 550°C for 0.3 seconds, which was repeated five times, to manufacture an aramid multifilament of 1500 denier/1000 filaments.

[170] Embodiments 2 to 5

[171] An aramid multifilament was manufactured by the same method as Embodiment 1, except that the concentrations of the sulfuric acid aqueous solution included in the coagulation solution of the coagulation bath (21) were 0.5%, 1.0%, 1.5%, and 2.0%, respectively.

[172] Comparative Examples 1 to 2

[173] An aramid multifilament was manufactured by the same method as Embodiment 1, except that the concentrations of the sulfuric acid aqueous solution included in the coagulation solution of the coagulation bath (21) were 0% and 3.5%, respectively.

[174] Embodiments 6 to 8

[175] An aramid multifilament was manufactured by the same method as Embodiment 1, except that the winding speeds were set to 800 m/min, 1200 m/min, and 1400 m/min, respectively.

[176] Comparative Examples 3 to 4

[177] An aramid multifilament was manufactured by the same method as Embodiment 1, except that the winding speeds were set to 600 m/min and 1600 m/min, respectively.

[178] Comparative Example 5

[179] An aramid multifilament was manufactured by the same method as Embodiment 1, except that the spun material was coagulated directly in the coagulation section (20) without passing it through an air gap (non-coagulable fluid layer).

[180] Embodiments 9 to 11

[181] An aramid multifilament was manufactured by the same method as in Embodiment 1, except that the shear rate (SR) and stretch factor (SF) were changed to the conditions shown in Table 1 below.

[182] Comparative Examples 6 to 7

[183] An aramid multifilament was manufactured by the same method as in Embodiment 1, except that the shear rate (SR) and stretch factor (SF) were changed to the conditions shown in Table 1 below.

[184] Table 1

Category	Shear rate (SR)	Stretch factor (SF)	Value (SR + 20,000 SF)
Embodiment 9	500,000	25	1,000,000
Embodiment 10	100,000	5	200,000
Embodiment 11	200,000	10	400,000
Comparative Example 6	10,000	1.5	40,000
Comparative Example 7	410,000	30	1,100,000

[185]

[186] The physical properties of each aramid multifilament manufactured by Embodiments 1 to 11 and Comparative Examples 1 to 7 were measured by the following methods, and the results are shown in Table 2.

[187] Modulus (g/d)

[188] The stress-strain curve of the sample is obtained under the above strength measurement conditions, and then they were calculated from the slope of the stress-strain curve.

[189] Static constant value

[190] Static constant value = C × D

[191] (In the above formula, C is the crystallinity of the aramid multifilament, and D is the density (g/cm^3) of the aramid multifilament. Meanwhile, the crystallinity was obtained

from the formula [(D-Da)/(Dc-Da)], where D is the density (g/cm^3) value measured using a density gradient tube, Da is the density value of the non-crystalline region, and De is the density value of the crystalline region.)

[192] Crystal orientation constant

[193] Crystal orientation constant = Xc × Fc

[194] (In the above formula, Xc is the crystallinity value of the aramid multifilament, and Fc is the orientation value of the aramid multifilament. The orientation value is obtained from the formula [f(010) + f(100)] / 2 using an X-ray device. However, f(010) and f(100) are obtained by averaging the orientation coefficients obtained from the width at 1/2 the height of the wide-angle diffraction pattern on the crystal planes of (010) and (100).)

[195] Table 2

Category	Sulfuric acid concentration (%)	Winding speed (m/min)	Whether or not it passed through the air gap	Modulus (g/d)	Crystallization constant value	Crystal orientation constant
Embodiment 1	2.5	1000	Passed	650	0.97	0.66
Embodiment 2	0.5	1000	Passed	420	0.91	0.52
Embodiment 3	1.0	1000	Passed	480	0.94	0.55
Embodiment 4	1.5	1000	Passed	530	0.95	0.61
Embodiment 5	2.0	1000	Passed	610	0.97	0.65
Comparative Example 1	0	1000	Passed	310	0.74	0.44
Comparative Example 2	3.5	1000	Passed	830	1.43	0.82
Embodiment 6	2.5	800	Passed	560	0.95	0.62
Embodiment 7	2.5	1200	Passed	690	0.98	0.67
Embodiment 8	2.5	1400	Passed	730	0.99	0.69
Comparative Example 3	2.5	600	Passed	350	0.85	0.46
Comparative Example 4	2.5	1600	Passed	930	1.43	0.82
Comparative Example 5	2.5	1000	Not passed	320	0.84	0.47
Embodiment 9	2.5	1000	Passed	720	0.98	0.67
Embodiment 10	2.5	1000	Passed	610	0.97	0.66
Embodiment 11	2.5	1000	Passed	660	0.97	0.67
Comparative Example 6	2.5	1000	Passed	310	0.83	0.45
Comparative Example 7	2.5	1000	Passed	870	1.43	0.82

[196]

[197] Next, an aramid tire cord is manufactured by the following method using the aramid multifilament manufactured according to the above method.

[198] Embodiment 12

[199] The aramid multifilament manufactured by Example 1 was subjected to z-twisting at a twist count of 30 turns/10 cm using a spinning device (Cable & Cord 3 type twister, Allma Co.), and two strands of the z-twisted yarn were then combined and s-twisted at a twist count of 30 turns/10 cm to produce a cabled yarn, which was then woven to produce a cord fabric.

[200] The above-mentioned cord material was immersed in an adhesive resin solution

containing 2.0 wt% of resorcinol, 3.2 wt% of formalin (37%), 1.1 wt% of sodium hydroxide (10%), 43.9 wt% of styrene/butadiene/vinylpyridine (15/70/15) rubber (41%), and water, and the pick-up ratio was adjusted to 5 wt% based on the aramid cabled yarn, and then dried at 150°C for 60 seconds and then heat-treated at 250°C for 120 seconds to manufacture an aramid tire cord.

[201] Embodiments 13 to 22

[202] An aramid tire cord was manufactured by the same method as in Embodiment 12, except that each aramid multifilament manufactured by the methods of Embodiment 2 to 11 was used.

[203] Comparative Examples 8 to 14

[204] An aramid tire cord was manufactured by the same method as Embodiment 12, except that each aramid multifilament manufactured by the methods of Comparative Examples 1 to 7 was used.

[205]

[206] The physical properties of each aramid tire cord manufactured by Embodiments 12 to 22 and Comparative Examples 8 to 14 were measured by the following methods, and the results are shown in Table 3.

[207] Initial modulus change rate (%)

[208] 25 cm long aramid tire cord samples as measured by Instron Engineering Corp. (Canton, Mass) according to the ASTM D-885 test method are used for measurement.

[209] First, the sample is subjected to tensile repetition 10 times at 120°C or 150°C under a load corresponding to 10% of the breaking strength to obtain a stress-strain curve, and the slope value of the stress-strain curve in the range where a load of 3 to 4 g/d is applied to the sample among the stress-strain curves is obtained and used as the initial modulus (M2) after the tensile repetition test.

[210] Next, a load is applied to another sample until it breaks at 25°C to obtain a stress-strain curve, and then the slope value of the stress-strain curve in the range where a load of 3 to 4 g/d is applied to the sample among the stress-strain curves is obtained and used as the initial modulus (M1) before the tensile repetition test.

[211] M1 and M2 obtained in this manner were substituted into Calculation Formula 1 below to measure the change rate of each initial modulus at 120°C or 150°C.

[212] [Calculation Formula 1]

[213] Initial modulus change rate (%) = $[(M1 - M2) / M1] \times 100$

[214]

[215] Strength retention rate (%)

[216] 25 cm long aramid tire cord samples as measured by Instron Engineering Corp. (Canton, Mass) according to the ASTM D-885 test method are used for measurement.

[217] First, the sample is subjected to tensile repetition 10 times under a load corresponding to 10% of the breaking strength at 120°C or 150°C, and then the sample is stretched again until it is judged to be at the point of break (g/d), which is measured to be referred to as the breaking strength after the tensile repetition test (S2).

[218] Next, another sample was stretched until it broke at 25°C and the strength at the point of break (g/d) was measured, which is referred to as the strength before the tensile repetition test (S1).

[219] S1 and S2 obtained in this manner were substituted into Calculation Formula 2 below to measure the strength retention rate at 120°C or 150°C.

[220] [Calculation Formula 2]

[221] Strength retention rate (%) = (S2 / S1) × 100

[222]

[223] Elongation strain rate (%)

[224] After leaving the aramid tire cord at 30°C or 120°C for 100 hours under a load corresponding to 20% of the breaking strength, the elongation strain rate at 30°C or 120°C was measured from Calculation Formula 3 below.

[225] [Calculation Formula 3]

[226] Elongation strain rate (%) = [(L1 - L0) / L0] ×100

[227] (In the above formula, L0 represents the length value of the aramid tire cord before applying a load, and L1 represents the length value of the aramid tire cord after being left for 100 hours under a load corresponding to 20% of the breaking strength of the aramid tire cord at 30°C or 120°C.)

[228]

[229] Initial modulus retention rate (%)

[230] 25 cm long aramid tire cord samples as measured by an Instron Engineering Corp. (Canton, Mass) instrument according to the ASTM D-885 test method are used for measurement.

[231] First, the sample is left at 25°C, 65RH% for 100 hours, and a stress-strain curve is obtained using an Instron instrument. Then, the slope value of the stress-strain curve in the range where a load of 3 to 4 g/d is applied among the stress-strain curves is obtained, and this is called the initial modulus (M'1) measured after leaving the sample at 25°C, 65RH% for 100 hours.

[232] Next, after leaving another sample at 80°C, 80RH% for 100 hours, a stress-strain curve is obtained using an Instron instrument, and then the slope value of the stress-strain curve in the range where a load of 3 to 4 g/d is applied among the stress-strain curves is obtained, and this is called the initial modulus (M'2) measured after leaving the sample at 80°C, 80RH% for 100 hours.

[233] M'2 and M'1 obtained in this manner were substituted into Calculation Formula 4 below to measure the initial modulus retention rate of the aramid tire cord.

[234] [Calculation Formula 4]

[235] Initial modulus retention rate (%) = (M'2 / M'1) × 100

[236]

[237] Breaking Strength Retention (%)

[238] 25 cm long aramid tire cord samples as measured by an Instron Engineering Corp. (Canton, Mass) instrument according to the ASTM D-885 test method are used for measurement.

[239] First, the breaking strength (g) was measured using an Instron instrument after leaving the sample at 25°C, 65RH% for 100 hours, and this was called the breaking strength (S'1) measured after leaving the sample at 25°C, 65RH% for 100 hours.

[240] Next, the breaking strength (g) was measured using an Instron instrument after leaving the sample at 80°C, 80RH% for 100 hours, and this was called the breaking strength (S'2) measured after leaving it at 80°C, 80RH% for 100 hours.

[241] S'2 and S'1 obtained in this manner were substituted into Calculation Formula 5 to measure the breaking strength retention of the aramid tire cord.

[242] [Calculation Formula 5]

[243] Breaking Strength Retention (%) = (S'2 / S'1) × 100

[244]

[245] Intermediate elongation (%)

[246] In accordance with the ASTM D-885 test method, the elongation change rate at the load point of 6.75 kg is obtained from the elongation-load graph measured on an Instron testing instrument (Instron Engineering Corp., Canton, Mass), and this was used as the intermediate elongation.

[247]

[248] Dry heat shrinkage rate (%)

[249] Using the shrinkage behavior tester (TestRite) in accordance with the ASTM D 4974-04 test method, measurements were made using the ratio of the length (L2) measured under a constant load of 0.01 g/d and the length (L3) after treatment at 180°C for 2 minutes under a load of 0.01 g/d.

[250] Dry heat shrinkage rate (%) = [(L2 - L3) / L2] × 100

[251] Table 3

Category	Initial modulus change rate (%)		Strength retention rate (%)		Elongation strain rate (%)		Initial modulus retention rate (%)	Breaking Strength Retention (%)	Intermediate elongation (%)	Dry heat shrinkage rate (%)
	120 degrees	150 degrees	120 degrees	150 degrees	30 degrees	120 degrees				
Embodiment 12	3	4	96	93	0.2	0.5	98	99	0.8	0
Embodiment 13	2	3	99	98	0.1	0.8	96	97	1.3	0
Embodiment 14	2	3	98	96	0.1	0.8	97	98	1.0	0
Embodiment 15	3	3	96	94	0.1	0.7	99	99	0.8	0
Embodiment 16	3	4	96	93	0.2	0.5	98	97	0.5	0
Embodiment 17	3	3	96	94	0.1	0.7	99	99	0.8	0
Embodiment 18	4	4	96	93	0.1	0.7	96	96	0.6	0
Embodiment 19	4	4	96	94	0.2	0.7	96	96	0.4	0
Embodiment 20	4	4	96	93	0.1	0.7	96	96	0.6	0
Embodiment 21	3	4	96	93	0.2	0.5	98	97	0.5	0
Embodiment 22	2	2	98	97	0.1	0.4	99	97	0.8	0
Comparative Example 8	6	8	91	88	0.6	1.3	91	92	1.9	0.5
Comparative Example 9	8	9	89	84	0.7	1.5	87	87	0.1	0.4
Comparative Example 10	7	9	87	84	0.7	1.6	87	86	2.0	0.6
Comparative Example 11	12	14	88	87	0.6	1.5	90	88	0.1	0.4
Comparative Example 12	13	14	85	81	0.9	1.7	83	81	1.7	0.5
Comparative Example 13	13	14	85	81	0.9	1.7	83	81	1.7	0.7
Comparative Example 14	12	14	88	87	0.6	1.5	90	88	0.1	5.1

[252]

Claims

[1] An aramid tire cord comprising an aramid multifilament,
characterized in that the initial modulus change rate is 5% or less after 10 tensile repetition tests under a load corresponding to 10% of the breaking strength at 120°C, as defined by Calculation Formula 1 below.
[Calculation Formula 1]
Initial modulus change rate (%) = [(M1 - M2) / M1×100
(In the above formula, M1 is the initial modulus (g/d) value before the tensile repetition test, and M2 is the initial modulus (g/d) value after the tensile repetition test.)

[2] The aramid tire cord according to Claim 1,
which is defined by Calculation Formula 1 above and characterized by having an initial modulus change rate of 5% or less after 10 tensile repetition tests under a load corresponding to 10% of the breaking strength at 150°C.

[3] The aramid tire cord according to Claim 1,
which is defined by Calculation Formula 2 below and characterized by having a strength retention rate of 95% or more after 10 tensile repetition tests under a load corresponding to 10% of the breaking strength at 120°C.
[Calculation Formula 2]
Strength retention rate (%) = (S2 / S1) × 100
(In the above formula, S1 is the strength (g/d) value before the tensile repetition test, and S2 is the strength (g/d) value after the tensile repetition test.)

[4] The aramid tire cord according to Claim 1,
which is defined by Calculation Formula 2 below and characterized by having a strength retention rate of 90% or more after 10 tensile repetition tests under a load corresponding to 10% of the breaking strength at 150°C.
[Calculation Formula 2]
Strength retention rate (%) = (S2 / S1) × 100
(In the above formula, S1 is the strength (g/d) value before the tensile repetition test, and S2 is the strength (g/d) value after the tensile repetition test.)

[5] The aramid tire cord according to Claim 1,
which is defined by Calculation Formula 3 below and characterized by having an elongation strain rate of 0.01 to 0.3% after being left for 100 hours under a load corresponding to 20% of the breaking strength at 30°C.
[Calculation Formula 3]
Elongation strain rate (%) = [(L1 - L0) / L0] × 100
(In the above formula, L0 represents the length value of the aramid tire cord before applying a load, and L1 represents the length value of the aramid tire cord after being left for 100 hours under a load corresponding to 20% of the breaking strength of the aramid tire cord at 30°C.)

[6] The aramid tire cord according to Claim 1,
which is defined by Calculation Formula 3 below and characterized by having an elongation strain rate of 0.3 to 1.0% after being left for 100 hours under a load corresponding to 20% of the breaking strength at 120°C.
[Calculation Formula 3]
Elongation strain rate (%) = [(L1 - L0) / L0] × 100
(In the above formula, L0 represents the length value of the aramid tire cord before applying a load, and L1 represents the length value of the aramid tire cord after being left for 100 hours under a load corresponding to 20% of the breaking strength of the aramid tire cord at 30°C.)

[7] The aramid tire cord according to Claim 1,
which is defined by Calculation Formula 4 below and characterized by having an initial modulus retention rate of 95% or higher.
[Calculation Formula 4]
Initial modulus retention rate (%) = (M'2 / M'1) × 100
(In the above formula, M'1 is the initial modulus (g/d) value of the aramid tire cord measured after leaving it at 25°C, 65RH% for 100 hours, and M'2 is the initial modulus (g/d) value of the aramid tire cord measured after leaving it at 80°C, 80RH% for 100 hours.)

[8] The aramid tire cord according to Claim 1,
which is defined by Calculation Formula 5 below and characterized by having a breaking strength retention of 95% or higher.
[Calculation Formula 5]
Breaking Strength Retention (%) = (S'2 / S'1) × 100
(In the above formula, S'1 is the breaking strength (g) value of the aramid tire cord measured after leaving it at 25°C, 65RH% for 100 hours, and S'2 is the breaking strength (g) value of the aramid tire cord measured after leaving it at 80°C, 80RH% for 100 hours.)

[9] The aramid tire cord according to Claim 1,
which is defined by Calculation Formula 6 below and characterized by having a crystallization constant value of 0.9 to 1.0.
[Calculation Formula 6]
Crystallization constant value = C × D
(In the above formula, C is the crystallinity of the aramid multifilament, and D is the density of the aramid multifilament (g/cm^3).)

[10] The aramid tire cord according to Claim 1, wherein the aramid multifilament is defined by Calculation Formula 7 below and characterized by having a crystal orientation constant of 0.5 to 0.7.
[Calculation Formula 7]
Crystal orientation constant = Xc × Fc
(In the formula above, Xc is the crystallinity value of the aramid multifilament, and Fc is the orientation value of the aramid multifilament.)

[11] The aramid tire cord according to Claim 1,
wherein the aramid multifilament is characterized by having a modulus of 400 to 750 g/d.

[12] The aramid tire cord according to Claim 1,
wherein the aramid multifilament is characterized by containing poly(para-phenylene terephthalamide).

[13] The aramid tire cord according to Claim 1,
which is characterized by having an intermediate elongation of 0.3 to 1.5% under a load of 6.75 kg.

[14] The aramid tire cord according to Claim 1,
which is characterized by having a dry heat shrinkage rate of 0.3 to -1.0%.

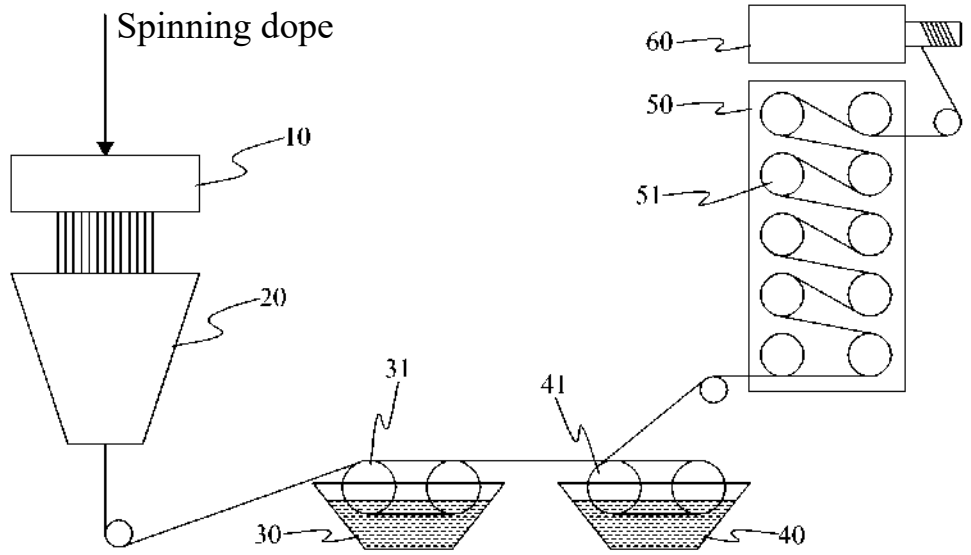
[15] A method for manufacturing an aramid tire cord, comprising: a step of spinning a spinning dope comprising an aromatic polyamide polymer;
a step of coagulating the spun material to form a multifilament;
a step of washing the multifilament; and
a step of drying and winding the washed multifilament, wherein the step of coagulating the spinning dope comprises a process of coagulation after passing the spinning dope through a hole in a spinneret, and then sequentially passing it through an air gap, a coagulation bath containing a coagulation solution containing sulfuric acid with a sulfuric acid concentration of 3% or less, and a coagulation tube, and wherein a shear rate (SR) in the spinneret and a stretch factor (SF) in the air gap satisfy Calculation Formula 8 below.
[Calculation Equation 8]
$50{,}000 \leq SR + (20{,}000 \times SF) \leq 1{,}000{,}000$
(Here, the shear rate (sec^{-1}) is a value obtained by dividing the speed (m/min) of the spinning dope passing through the hole of the spinneret by the diameter (μm) of the hole of the spinneret, and the stretch factor is a value obtained by dividing the speed (m/min) of the filament emitted from the coagulation tube by the speed (m/min) of the spinning dope emitted from the hole of the spinneret.)

[16] The method for manufacturing an aramid tire cord according to Claim 15,
wherein the distance from the top of the coagulation solution stored in the coagulation bath to the nozzle provided in the coagulation tube is in the range of 10 to 35 mm.

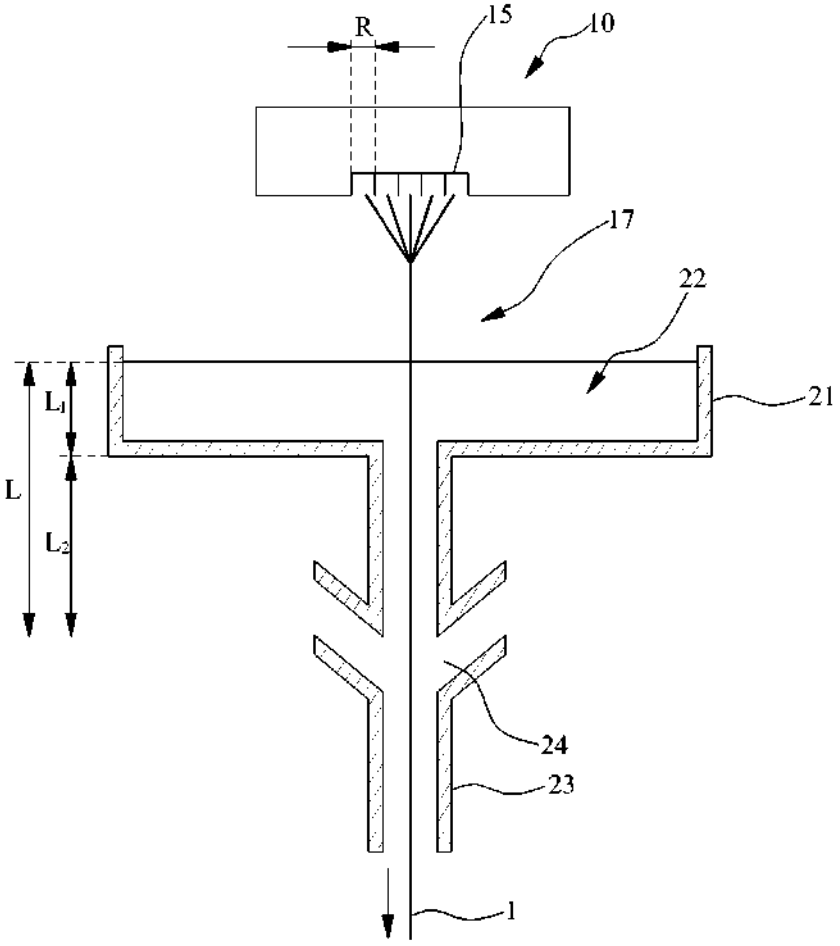
[17] The method for manufacturing an aramid tire cord according to Claim 15,
wherein through the above-mentioned winding step, the dried multifilament is wound at 700 to 1,500 m/min.

[18] The method for manufacturing an aramid tire cord according to Claim 15, comprising the steps of:
manufacturing an aramid cabled yarn from the manufactured aramid multifilament;
immersing the aramid cabled yarn in an adhesive resin solution containing resorcinol-formaldehyde-latex (RFL);
drying the immersed aramid cabled yarn at 105 to 200° C. for 10 to 400 seconds; and
heat-treating the dried aramid cabled yarn at 105 to 300° C. for 10 to 400 seconds.

[Fig. 1]


Spinning dope
10
20
60
50
51
31
41
30
40

[Fig. 2]


R
15
10
17
22
21
L1
L
L2
24
23
1